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Guidelines for Stack Testing at Municipal Waste Combustion Facilities

Midwest Research Inst., Kansas City, MO

Prepared for

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16. ABSTRACT The report gives guidance for stack testing at municipal waste combustion (MWC) facilities. State and local environmental agencies have been required to develop regulations for MWCs in response to a significant expansion in the number of MWC facilities currently in operation or in some phase of planning and construction. As part of this regulatory process, permitting agencies need guidance on identifying critical emission parameters and on methods that can be used to measure those parameters, expecially toxic substances. The Northeast States for Coordinated Air Use Management (NESCAUM), with support from EPA's Control Technology Center, organized a work group of recognized experts to provide specific guidance on methods for measuring stack emissions from MWCs and reporting formats to facilitate standardization of emissions tests. This methods guidelines report is based on the discussions of the NESCAUM work group. Specific testing recommendations, emissions, measurement methods, and recommended reporting formats are presented. These recommendations are not intended to prescribe regulatory requirements, but to recommend emissions test programs responsive to typical requirements. The measurement methods presented are based primarily on reference methods already in widespread use.

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This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

This report was prepared under EPA Contract No. 68-02-4395, Work Assignment 4. The objective of this work assignment was to assist the U.S. Environmental Protection Agency (EPA) Control Technology Center (CTC) and the Northeast States for Coordinated Air Use Management (NESCAUM) in developing a methods guidance document for testing municipal waste combustors (MWCs).

A Work Group was organized by NESCAUM to address issues in MWC testing. The overall goal of the Work Group is to provide state and local agencies permitting MWCs agencies with guidance on testing methods and reporting formats. The specific objectives of the Work Group are as follows:

1. Develop standardized MWC stack test methods;

2. Develop standardized reporting formats for MWC test results;

3. Identify unresolved stack testing technical issues; and

4. Promote exchange of technical information on MWC stack testing.

This methods document is the product of the Work Group's efforts to achieving these objectives.

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ACKNOWLEDGMENTS

This methods document is based on discussions by a Work Group organized by the Northeast States for Coordinated Air Use Management (NESCAUM). The Work Group was created to provide State and Local Agencies responsible for permitting municipal waste combustors (MWCs) with guidance on testing methods and formats for reporting test results. Nancy L. Seidman, Special Projects Director for NESCAUM, served as Project Manager. The Work Group members were drawn from State and Local Agencies, Federal Agencies in the United States and Canada, firms operating MWC facilities, and liaisons from professional organizations. The members of the Work Group are listed below.

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Clarence L. Haile of Midwest Research Institute and Judith C. Harris of Arthur D. Little, Inc., moderated and participated in the Work Group discussions and prepared this document.

We gratefully acknowledge the time invested by the Work Group. Their assistance and expertise made this project possible.

GUIDELINES FOR STACK TESTING OF MUNICIPAL WASTE COMBUSTION FACILITIES

SECTION 1.0

INTRODUCTION

Considerable interest and activity have recently been focused on assessing emissions from municipal waste combustors (MWCs). In particular, state and local environmental agencies have been required to develop regulations for MWCs in response to a significant expansion in the number of MWC facilities currently in operation or in some phase of planning and construction. As part of this regulatory process, permitting agencies have need for guidance on identifying critical emission parameters and also for methods that can be used to measure those parameters, especially toxic substances.

The Northeast States for Coordinated Air Use Management (NESCAUM) with the support of the U.S. Environmental Protection Agency (EPA) Control Technology Center (CTC) organized a work group to provide specific guidance on methods for measuring stack emissions from MWCs and reporting formats to facilitate standardization of emissions tests. This methods guidelines report is based on the discussions of the NESCAUM Work Group. Specific testing recommendations, emissions, measurement methods, and recommended results reporting formats are presented in the following sections.

The test recommendations presented in Section 2.0 are based on the Work Group's knowledge of current requirements of EPA and state and local permitting agencies and in anticipation of requirements likely to be imposed in the near future. These recommendations are not intended to prescribe regulatory requirements, but to recommend emissions test programs responsive to typical requirements.

The measurement methods presented in Section 3.0 are based primarily on reference methods already in widespread use, although few have been validated specifically for MWC testing. Most refer to EPA methods contained in the *Federal Register* and/or EPA methods manual for solid wastes (SW-846). However, many method recommendations and descriptions of critical method features specific to MWC emissions testing were drawn from the considerable knowledge and broad experience of the Work Group.

Section 4.0 of this document presents emission test reporting formats developed by the Work Group to encourage standardization of data reporting to both facilitate efficient emissions assessment and improve the usefulness of MWC test reports for comparing emissions among facilities. Standardized reporting can greatly facilitate use of test results to meet the needs of multiple users, e.g., risk assessment, modeling, and MWC research. For example, the Work Group recommends the use of 7% O_2 as the basis for normalizing stack gas concentrations to a common excess air level, although it recognizes that 12% CO_2 is frequently specified in permit limitations. There are advantages and disadvantages to both choices but the Group felt that one approach should be selected to increase consistency of reporting. In those cases there the applicable permit condition, emission limitation, or regulation specifies reporting units that are different from the NESCAUM recommended format, the Work Group recommends that results be reported both ways.

References for specific method citations are provided in Section 5.0. Section 6.0 is a bibliography of useful references for MWC testing.

Two appendices are included with the document. Appendix A provides additional measurement methods for MWC research testing. Appendix B provides selected detailed procedures for measuring PCDDs and PCDFs.

SECTION 2.0

TEST RECOMMENDATIONS

Stack testing at MWCs may be undertaken to address many different types of needs. The specific objectives of an MWC stack test can determine both the process and emission parameters to be measured and the methods appropriate to conduct the measurements. It is important at the outset of any testing program that all parties involved (facility owner/operator, regulatory bodies, organization performing the test, intervenors if any) have a common agreement on the measurements to be made and the use to be made of the data. It is also important to recognize that many potentially useful sampling and analysis methods may not have been validated for specific application to MWC testing. In those cases, extraordinary quality assurance and control procedures may be required in order to document the validity of the test results.

Conceptually, it is useful to categorize MWC stack testing (measurements) into four broad categories.

- Regulatory compliance testing - Testing to determine compliance with specific emission limitations imposed as permit conditions by federal, state, or local regulations (or guidelines), or by the terms of the individual facility permit.

- Performance testing - Testing to characterize emissions of a specific MWC unit or component, or to verify performance in accordance with an equipment vendor's guarantee.

- Research and development testing - Testing to develop data bases on MWC emissions, to determine the influence of specific operating parameters on emissions, and/or to characterize general classes of MWCs.

- Continuous monitoring - Testing of selected parameters on a continuous basis using instrumental monitors, to confirm that bulk combustion conditions and/or air pollution control device performance are not substantially different from those observed during initial compliance/performance testing.

The NESCAUM Work Group decided that this document should focus on the first three of these categories: Compliance testing, performance testing, and research and development testing. The group recognized that there are also important issues to be resolved in the area of continuous emission monitors (CEM), but felt that should be the subject of a separate, dedicated effort. The Work Group also determined that procedures for sampling and analysis of refuse, which have been the subject of investigations by the National Bureau of Standards, ASME, and others, were beyond the scope of this project document. A major objective of the NESCAUM project was to specify a set of "core" measurement procedures that could be applied consistently to MSW combustor testing by the various federal, state, and local jurisdictions. This will facilitate comparisons among facilities and lead to the generation of a more useful data base on MWC emissions.

2.1 COMPLIANCE TESTING

The objective of compliance testing is to determine whether an MWC is meeting all of the conditions regarding emissions that are imposed by its operating permit. In this context, the term "compliance" is used to refer not only to limits imposed by regulations, but to any other restrictions that may be imposed, on a case-by-case basis, in the operating permit for a facility. Typically, testing to determine compliance with all permit conditions is required at least one time during the first 6 months of facility operations, after the shake-down phase is complete. Some states are requiring follow-up compliance testing at intervals of 3 months to 1 year during the first years of operation, and annually or semiannually thereafter. The follow-up testing may not require the full range of measurements made during the initial compliance testing. Depending on the initial test results, a set of parameters considered to be key indicators of continuing compliance may be specified.

The parameters to be measured during compliance testing will depend, of course, on the emission limitations written into each individual permit. Based on their common understanding of current permit requirements imposed by Federal and, more importantly, state regulations, the NESCAUM Work Group determined that the following parameters are likely to be required in compliance testing for most new MWCs. It should be emphasized that this is not an exclusive list of parameters for compliance testing. Many state and local governments impose additional requirements for compliance.

- Polychlorinated dibenzodioxins and dibenzofurans including tetra- through octachloro homologs and/or all individual isomers containing chlorines at the 2,3,7, and 8-positions;
- Total hydrocarbons (THC);
- Metals including lead, mercury, cadmium, and total chromium;
- Combustion gases including carbon monoxide. carbon dioxide, and oxygen;
- Particulate matter and opacity;
- Other gases including hydrochloric acid (HCl), nitrogen oxides (NO_x), and sulfur dioxide (SO_2) as an indicator of SO_x; and
- Process operating conditions, including furnace and boiler data, emissions control device data.

Measurement methods for the stack test parameters are presented in Section 3.0 of this document.

It should be noted that the numerical limits on emissions of the above parameters will vary on a case-by-case basis. Even for particulate matter, covered by Federal EPA New Source Performance Standards (NSPS) for MWCs of 0.08 gr/SCF at 12% CO_2, new facility permits by the states are generally limiting emissions to levels of 0.015 or 0.010 gr/SCF. Similarly, different states have different criteria for setting PCDD/PCDF emission limitations.

The critical numerical limits for each measured parameter should be established before compliance testing plans are finalized. This will enable the measurement methods to be tailored, if necessary, to ensure that the method detection limits are appropriate for the permit emission limit.

The criteria that will be used to judge the acceptability of the compliance test results must also be carefully defined and documented. Compliance testing typically requires a minimum of three replicate tests under

the same nominal operating conditions. However, different agencies may have different quality assurance criteria regarding completeness. Some require that at least three tests be successfully completed for all parameters of concern. Others will accept the results even if one sample run is lost (e.g., laboratory error/accident) as long as the two tests successfully completed demonstrate compliance. The standard of completeness and contingency provisions, if any, should be discussed with regulatory authorities prior to testing. Requirements for analysis and reporting of results for QA audit samples, if any, should also be specified in advance of emissions testing.

The conditions tested should include the measurement of stack emissions at or near 100% of the design heat input capacity expected during normal operations if this is substantially different from the design capacity. If the facility wishes its operations to be permitted under lower refuse loads (e.g., 80% of design capacity), additional tests should be made using these operating conditions. For compliance testing, the furnace temperature, excess air, pressure drop across the boiler, air pollution control device parameters, etc., should be typical of those expected in routine operation. (Tests to determine the impact of these parameters on facility emissions are classified as research and development testing.)

In facilities consisting of multiple units of the same design (i.e., 750 TPD facility with three 250 TPD units), it is the consensus of the NESCAUM Work Group that bulk combustion parameters (e.g., particulate, CO, CO_2, O_2) should be measured on each unit. The parameters the group describes as "fuel-related," such as HCl, SO_2, trace organics and trace metals, need only be measured on one of the units, assuming they are of the same design and operated under the same nominal conditions. Note: These are the NESCAUM Work Group recommendations; some regulatory authorities may require additional testing on each unit.

2.2 PERFORMANCE TESTING

The objective of emissions performance testing is to determine whether a facility is operating in accordance with its design specifications, in contrast to compliance testing for comparison with emission limitations. Thus, while compliance testing usually involves sampling of the final stack effluent, performance testing may require sampling both upstream and downstream of air pollution control devices.

The parameters to be measured in performance testing could include any of those listed under compliance testing. In addition, there could be interest in, for example, comparison of control device efficiencies with respect to fine particulate matter (e.g., 10 or 2.5 μm mean cut diameter) or to specific organic or inorganic chemicals such as those listed below under research and development testing. The NESCAUM Work Group is not aware of any parameters uniquely associated with performance testing. Therefore, there are no methods in this document directed specifically to performance testing. The methods described under compliance and research and development testing can also be applied for performance testing.

The test conditions for performance testing again would depend upon what aspect of system performance was being determined. Operating parameters such as ESP electrical field, fabric filter cloth-to-air ratio (net or gross), or dry scrubber injection rate are examples of variables that might be controlled in performance testing. As

in compliance testing, a minimum of three runs at each condition of interest should be completed successfully to ensure that the results are representative of actual performance during the test period.

2.3 RESEARCH AND DEVELOPMENT TESTING

As in the case of performance testing, the objectives of research and development testing may be many and varied. Among the possibilities discussed by the NESCAUM Work Group are:

- Development of improved data bases through research and development which will help determine if additional parameters should be subjected to compliance testing or dropped from the current list of compliance pollutants,

- Expansion of the data base on refuse-derived fuel (RDF) facilities to determine whether apparent differences in emissions between mass burn and RDF combustion or among different RDF combustion systems are characteristic (generic) differences in the technologies or facility (waste)-specific phenomena, or

- Tests, possibly including measurements upstream of air pollution control devices, to assess the effects of controllable combustion parameters on emissions of specific pollutants,

- Tests of the hypothesis that PCDD/PCDF are formed primarily by post-combustion zone reactions,

- Evaluation of new combustor technologies,

- Evaluation of new or improved sampling and analysis methodologies.

Among the parameters that the NESCAUM Work Group identified as potentially of interest in MWC research and development sampling are the following:

- Volatile organics on a compound-specific basis, as contrasted with the aggregate measurement represented by THC. The testing may be directed toward target compounds, e.g., formaldehyde, or to a broad range gas chromatography/mass spectrometry (GC/MS) screen,

- Polychlorinated biphenyls including mono- through decachloro- homologs,

- Semivolatile organics possibly including chlorinated benzenes, chlorinated phenols, and polynuclear aromatic hydrocarbons (e.g., benzo[a]pyrene),

- Metals possibly including arsenic, beryllium, chromium (VI) versus total chromium, nickel. Research and development testing could also include multiple metals screening analysis.

Test conditions for research and development testing are likely to be even more variable than in the case of performance testing. These might include, for example, deliberate operation of a facility outside of its design specifications to define the envelope of acceptable vs unacceptable operation or to determine maximum emissions under worst case operating conditions. The comments made under compliance and performance testing also apply to research and development testing. In the case of some research and development testing, however, it may be necessary to perform six or more tests (vs the minimum of three specified earlier) at each condition in order to detect differences between emissions under different conditions.

Procedures potentially suitable for MWC research and development testing are presented in Appendix A. It should

be noted that many of these procedures were initially developed for purposes other than MWC testing, and may not have been validated for this purpose. It may be necessary to incorporate sufficient quality assurance and control measures in the test design to ensure that the method performance is adequate to meet the test objectives.

2.4 SPECIAL PURPOSE TEST PARAMETERS

Some MWC tests include test parameters selected because of local environmental concerns and special research requirements. The Work Group discussed several parameters in this category, but decided not to include measurement methods for them in this document.

For example, monochloro through trichloro dioxin and furan homologs were excluded primarily because homologs with less than four chlorines are not significant in determining risk factors according to most commonly used risk assessment protocols. The methods described for tetrachloro- through octachloro-PCDDs and PCDFs in Section 3.1 could be extended to the lower homologs, provided that the QC protocols are amended to include these categories.

Also, procedures for pollutants that are of concern only in limited localities or with infrequently used technologies (i.e., ammonia emissions possibly associated with slippage in de-NO_x technologies) were also omitted.

SECTION 3.0

MEASUREMENT METHODS FOR COMPLIANCE/ PERFORMANCE TESTING

3.1 POLYCHLORINATED DIBENZO-p-DIOXINS AND DIBENZOFURANS

The methods described in this section are appropriate for measuring tetrachloro through octachloro polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) in MWC stack emissions. The tetrachloro through octachloro homologs can be determined or the specific 2,3,7,8-substituted congener can be determined simultaneously with the homologs. Alternatively, 2,3,7,8-tetrachlorodibenzo-p-dioxin (2,3,7,8-TCDD) may be determined alone. Analysis of sample extracts for 2,3,7,8-TCDD or all 2,3,7,8-substituted congeners requires significantly more chromatographic separation than is required for homolog measurements only. Achieving the higher chromatographic resolution requires a longer analysis time, with proportionately higher analysis costs.

3.1.1 Method Description

Stack emission samples are collected for PCDD and PCDF measurement using an EPA Method 5 train modified by the addition of a condenser to cool the gases and an adsorbent cartridge to trap organics. This sampling train is generally referred to as a Modified Method 5 (MM5). Particulates are collected in the filter and vaporous emissions are retained by the cartridge. The distribution of PCDDs and PCDFs between the particulate catch and the cartridge are likely altered during sampling. However, the sum of PCDDs and PCDFs collected by the train represents the total concentrations in the stack emissions. Following sampling, the appropriate components of the train are recovered and transferred to the laboratory for analysis. The components are extracted, the extracts are cleaned to remove excessive levels of potential interferences, and the cleaned extracts are analyzed for PCDDs and PCDFs using combined gas chromatography/mass spectrometry (GC/MS).

3.1.1.1 Sample Collection--

A detailed protocol for collecting stack emissions using a MM5 sampling train can be found in Method 0010 of SW-846. This protocol was prepared specifically for measuring semivolatile organics in hazardous waste incinerator stack emissions to allow determination of destruction and removal efficiencies (DREs) of Principal Organic Hazardous Components (POHCs) contained in the waste feed. Method 0010 can be applied nearly directly for measuring PCDD and PCDF emissions since PCDDs and PCDFs are categorized as semivolatiles. The Method 0010 protocol is similar to the draft protocols produced as a result of a workshop sponsored by the American Society of Mechanical Engineers and U.S. Environmental Protection Agency, generally referred to as the ASME Draft Protocol (1984).

Train configuration. The MM5 train is assembled and operated in a manner very similar to a Method 5 particulate train with three exceptions:

a. Addition of a condenser and water-cooled adsorbent resin cartridge immediately downstream of the filter box.

b. The train precleaning to avoid organic contamination.

c. Sample recovery procedures.

A schematic of the MM5 sampling train from Method 0010, SW-846 is shown in Figure 3-1. The adsorbent cartridge is filled with Amberlite® XAD-2 resin specially precleaned according to the protocol contained in Method 0010, Appendix B, SW-846. The condenser and adsorbent cartridge can be fabricated as a single unit (as shown in Figure 3-2) or as individual units (Figure 3-3). The condenser cools the gas to 20°C or less and condenses part of the moisture. The cooled gases and condensed moisture flow down through the XAD-2 resin which retains PCDDs and PCDFs from the vaporous and aqueous phases.

Train assembly and operation. All train components from the first impinger forward must be rigorously cleaned before use to avoid organic contamination. The train should be assembled as shown in Figure 3-1. A cyclone (also precleaned) may be installed for sampling flue gas with high particulate loading, e.g., inlet of a particulate control device. Also, an oversized first impinger or additional impingers may be used to increase the water collection capacity for sampling high moisture gases, e.g., outlet of a wet scrubber.

The flue gas sample should be collected by operating the train according to the Method 5 specifications, including leak checking, isokinetic sampling rates, and stack or duct traversing. However, additional leak checks should be conducted after each port change. The sample should be in the range of 3 to 6 cubic meters.

Sample recovery. At the completion of sampling, the probe and umbilical should be carefully removed from the train, the ends of the probe and the train should be capped with precleaned aluminum foil or glass caps, and the probe and train should be removed to a clean field or permanent laboratory for sample recovery. The sample recovered consists of the following:

a. Front half rinse--rinse of the probe, front half of the filter holder, and rinse of connecting lines between the probe and filter holder (including a cyclone if used).

b. Particulate catch--filter, including cyclone catch (if used.)

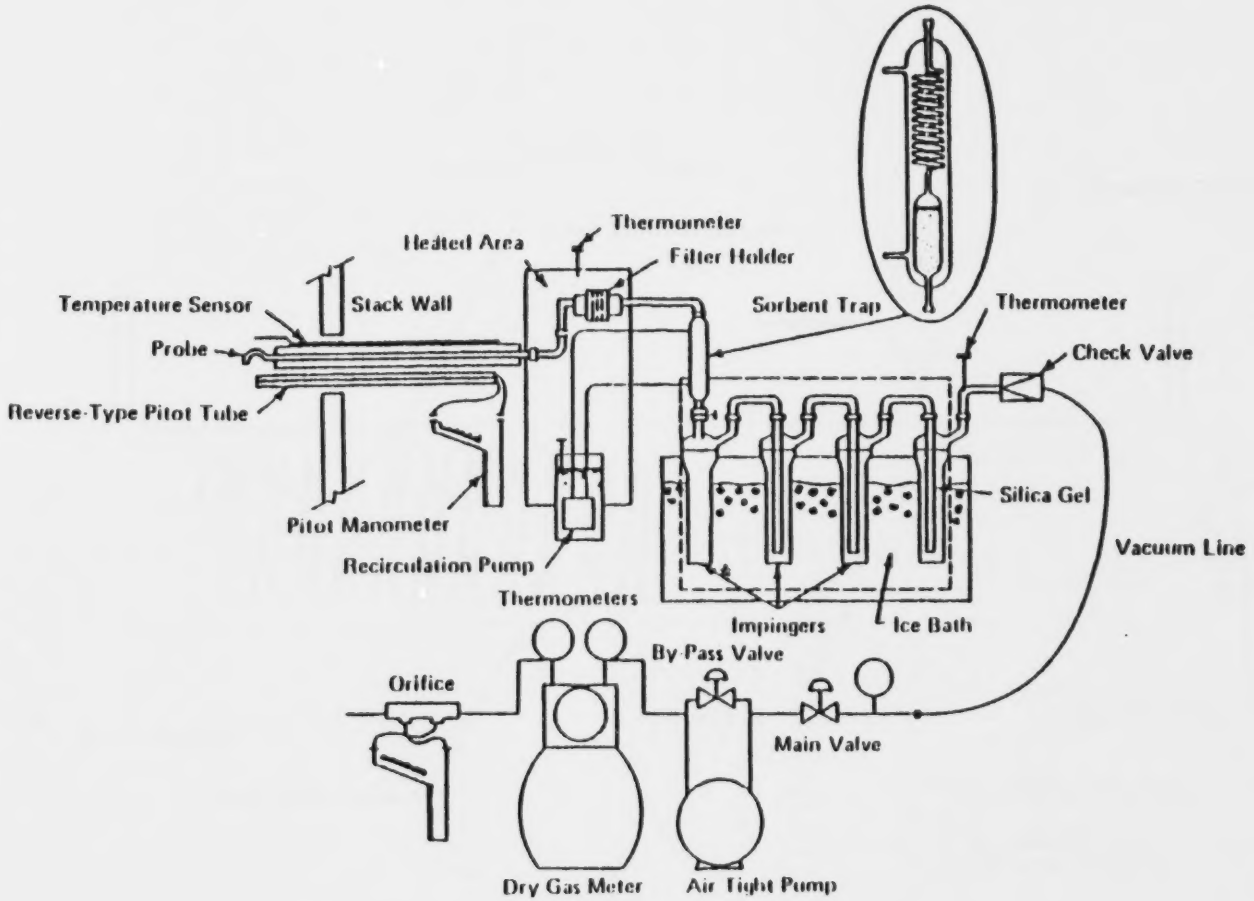

Figure 3-1. Modified Method 5 sampling train.
(from Method 0100, SW-846)

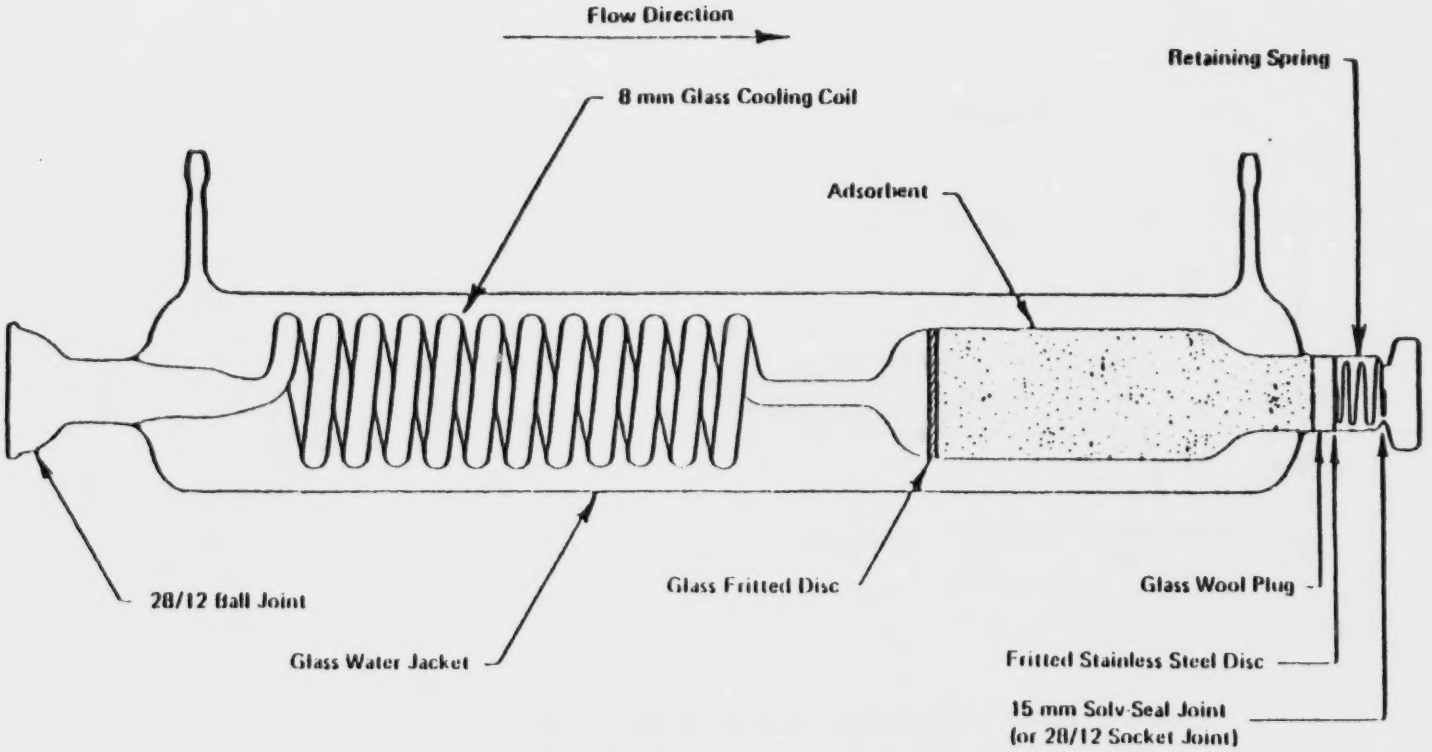

Figure 3-2. Combined condenser - adsorbent cartridge unit.
(from Method 0010, SW-846)

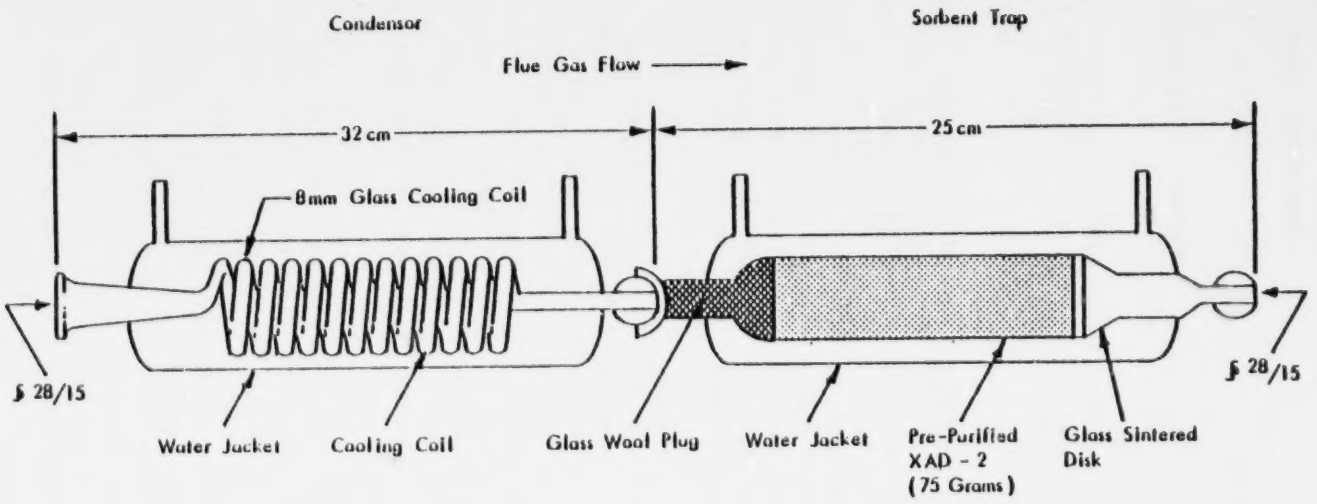

Figure 3-3. Separate condenser and adsorbent trap units train. (from Stanley, J. S., et al., EPA Report No. 560/5-82-014)

c. Back half rinse--rinses of back half of the filter holder and all connecting lines from the filter holder to the inlet of the resin cartridge.

d. Resin cartridge.

e. First impinger--condensed sample moisture.*

A detailed procedure for each train component is presented in Appendix C.

3.1.1.2 Sample Analysis--

A detailed protocol for analyzing PCDDs and PCDFs in a wide range of sample types can be found in Method 8280 of SW-846. Although much of this protocol can be applied directly for determining these compounds in samples recovered from MM5 trains, some modifications are typically required to achieve method detection limits suitable for MWC stack samples.

Sample preparation and extraction. Solid sample components, i.e., the filter and cyclone (if used) catch and the XAD-2 resin are Soxhlet extracted using toluene or benzene. The aqueous components and rinses are extracted by simple partitioning with dichloromethane. A detailed procedure for extracting each train component is presented in Appendix C.

Prior to extraction, the samples must be spiked with solution of method internal standard (MIS) compounds. These are isotopically labeled PCDD and/or PCDF congeners (sometimes referred to as surrogate compounds) which are used to quantitate PCDDs and PCDFs in the sample by an internal standard method. If available, it should also contain a labeled congener representing each homolog quantitated. A typical MIS solution might contain the following:

$^{13}C_{12}$-2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin)
$^{13}C_{12}$-1,2,3,7,8-PeCDD (pentachlorodibenzo-p-dioxin)
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD (hexachlorodibenzo-p-dioxin)
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD (heptachlorodibenzo-p-dioxin)
$^{13}C_{12}$-OCDD (octachlorodibenzo-p-dioxin)

Extract cleanup. The extracts from the individual train components should be combined, concentrated, and cleaned by column chromatography as described in Method 8280 to remove coextracted interferences. The final, cleaned extract should be prepared in a high boiling solvent, such as tridecane or hexadecane. Achieving very low detection limits typically requires a final extract volume in the range of 15 to 100 µL. A detailed procedure for extract cleanup is presented in Appendix C.

GC/MS analysis. Sample extracts must be analyzed by GC/MS as described in Method 8280, SW-846 using a fused silica capillary column and selected ion monitoring (SIM) data acquisition. The GC/MS system must provide sufficient chromatographic separation and a level of sensitivity sufficient to achieve the desired minimum detection limits for all subject compounds.

The PCDDs and PCDFs are quantitated using response factors normalized to the MIS compounds spiked prior to sample extraction. A detailed procedure for GC/MS analysis, including guidance on instrument specifications

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* The condensate may be analyzed separately to provide an indication of gross breakthrough.

and GC column selection, is presented in Appendix C.

The GC/MS calibration standard solutions should contain the following:

a. A native congener representative of each PCDD or PCDF homolog to be quantitated, at one of the three calibration levels.

b. The MIS compounds at levels corresponding to that spiked into the samples, i.e., equivalent to 100% recovery.

c. At least one recovery internal standard compound (RIS), to be used to determine the recoveries of the MIS compounds, at a level similar to the MIS compounds.

An example of the compounds included in a calibration standard for determining 2,3,7,8-substituted PCDDs and PCDFs is presented in Table 3-1.

3.1.2 Critical Features

3.1.2.1 Sample Collection--

Sampling train materials. All sampling train components that come in contact with the recovered sample must be composed of glass, polytetrafluoroethylene (PTFE), or similar materials to avoid potential sample contamination or reactions with PCDDs and PCDFs. Hence, the probe liner must be of borosilicate glass or quartz. Also, the probe nozzle should be nickel or nickel plated or (if available) constructed of glass or quartz. If the location and/or orientation of the sampling ports requires, a short PTFE flexible line may be used to connect the probe to the filter (or cyclone, if used) inlet. However, the internal diameter of the line must be the same as the probe liner and the line must be heated to retard condensation of moisture.

Gaskets or other joint seals fabricated from materials other than PTFE should not be used. This includes the filter gasket. The use of silicone sealant greases is not permitted. The use of silicone sealant greases and other materials on train components not contacting the sample is acceptable but not advised.

Condenser/resin cartridge unit. Alternate configurations for the condenser and resin cartridge may be acceptable. However, the units must be configured so that flue gas and condensed moisture flows down through the resin and the cartridge should be charged with 20 to 80 g of XAD-2 resin (40 g is typical). Figure 3-4 shows an alternate configuration with the condenser and resin cartridge designed in the shape of impingers to reduce the height of the train and decrease the potential for breakage during handling. Although the appearance of this configuration is very different from those shown in Figures 3-2 and 3-3, the unit is acceptable because the condensed moisture is required to flow down through the resin and the capacity of the cartridge is 65 g of resin. During sample recovery, any condensed moisture collected in the bottom of the condenser unit is poured through the XAD resin.

Also, the quality of the resin must be checked before packed cartridges are used. At least one aliquot of each resin lot (manufacturers and cleanup batch) equivalent to a cartridge charge should be extracted and analyzed as a sample to confirm the background levels of the compounds of interest or potential interferences are acceptable.

TABLE 3-1. LIST OF ANALYTES, METHOD INTERNAL STANDARDS, SURROGATES, AND RECOVERY INTERNAL STANDARDS FOR DIOXIN/FURAN ANALYSIS

Analyte	Compounds in calibration standard	Method internal standard[a]	Recovery internal standard[b]
Tetra-CDD	2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	$^{37}Cl_4$-2,3,7,8-TCDD or
Tetra-CDF	2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
Penta-CDD	1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	
Penta-CDF	1,2,3,8,9-PeCDF	$^{13}C_{12}$-1,2,3,8,9-PeCDF	
Penta-CDF	2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDD	
Hexa-CDD	1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
Hexa-CDD	1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDD	1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDF	1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDF	1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDF	2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDF	1,2,3,4,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hepta-CDD	1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	
Hepta-CDF	1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	
Hepta-CDF	1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	
Octa-CDD	OCDD	$^{13}C_{12}$-OCDD	
Octa-CDF	OCDF	$^{13}C_{12}$-OCDD	

[a] Added to sample prior to extraction.

[b] Added to sample at time of injection into GC/MS.

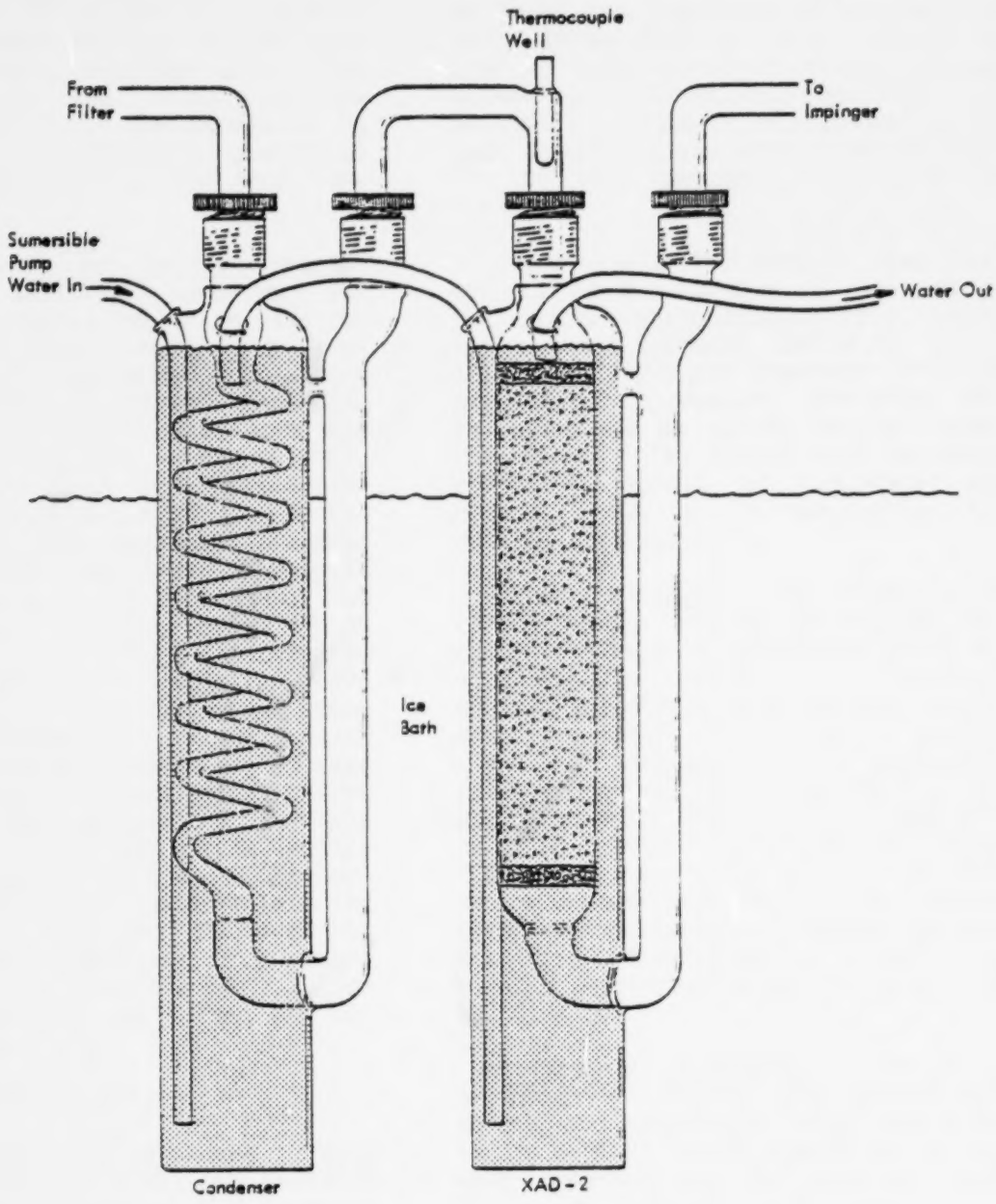

Figure 3-4. Example condenser and XAD resin cartridge designed in impinger form.

Resin cartridge temperature. Care must be taken during sample collection to ensure proper cooling of the condenser and resin cartridge unit. The temperature at the inlet to the cartridge should not be permitted to exceed 20°C. Considerable quantities of ice may be required for each sampling run.

Use of sample for multiple parameters. Some additional parameters can be determined from a MM5 train used for PCDD and PCDF measurements, with varying degrees of compromise. Solutions charged into the second and succeeding impingers may be modified to facilitate analysis of compounds such as HCl. Aliquots of the first impinger solution can also be utilized. Also, the extract(s) from train components prepared for PCDD and PCDF analysis can be split for use in determining other semivolatile organics. However, splitting of the extract proportionately increases the minimum detectable levels for PCDDs and PCDFs as well as the other semivolatile parameters. The particulate catch from the train should not be used to measure particulate emissions. Drying the filter to achieve reliable gravimetric analysis may result in significant losses of PCDDs and PCDFs contained on the filter. Similarly, the filter should not be aliquoted to facilitate other analyses, e.g., nonvolatile metals, since the distribution of particulates on the filter may not be uniform.

3.1.2.2 Sample Analysis--

Method internal standard (MIS) spiking. The potential for reliable quantitation of a PCDD of PCDF compound may be significantly enhanced using an MIS compound with very similar chemical and physical properties. Unfortunately, the availability of appropriately mass labeled PCDD and PCDF congeners limits the number of MIS compounds that can be practicably used in MWC stack measurements. Nonetheless, at least two compounds, a labeled TCDD and labeled OCDD or OCDF, should be used to quantitate tetrachloro through octachloro PCDD and PCDF homologs. If possible, a labeled representative of each homolog class should be included in the MIS compounds, e.g., as in Table 3-1.

In the case of MM5 samples, the final extract is a composite of extracts of the several train components. Hence, any one MIS compound should be spiked into only one train component prior to extraction. However, different MIS solutions can be spiked into different components. The filter and XAD resin components should be considered the highest priority in developing MIS spiking strategies.

Extract cleanup. The alumina and carbon column cleanup procedures require considerable laboratory skill and attention to detail to routinely achieve acceptable PCDD and PCDF recoveries and a sufficient level of extract cleanup. Laboratory staff conducting these procedures should be familiar and practiced with the adsorbents and with handling trace quantities of PCDDs PCDFs. Laboratories conducting PCDD and PCDF analyses should have demonstrated acceptable recoveries by processing spiked blanks through the cleanup procedures prior to analysis of MWC samples.

Quality of standards. Analytical standards for natives and labeled congeners are expensive. They are typically sold in small quantities of the neat compound or in solution form. Both the purity and quantitative accuracy of standard solution should be evaluated before use. At the very least, the origin and use of standards solutions should be clearly traceable.

Handling of small extract volumes. Achieving optimum detection limits for PCDDs and PCDFs typically requires concentrating the final extract to considerably less than 1 mL. It is very important that small volume extracts be handled with extreme care. Whenever possible, maintain the extracts at larger volumes until just before GC/MS analysis and concentrate to less than 500 µL only in the presence of a higher boiling keeper solvent, e.g., tridecane or hexadecane. Also, do not attempt to split or aliquot extracts at volumes less than 1.0 mL. Dilute the extract, split or aliquot are required, then reconcentrate as needed.

Selection of a GC/MS system. The principal considerations are the basic sensitivity of the instrument, the effective SIM mass range during analysis, and the mass resolution. The instrument level of detection required should be calculated from the target detective level in the flue gas sample.

The various spectrometer systems have different capabilities and limitations. Quadrupole focusing mass spectrometers can provide good sensitivity for the entire range of ions required to determine tetrachloro through octachloro PCDDs and PCDFs in a single GC/MS run. Also, the set of ions monitored can be changed under computer control during the run. The effective SIM range of magnetic focusing mass spectrometers is limited because the sensitivity inherently falls off at higher mass for a fixed magnet setting. It is generally not practical to change magnet settings during a GC/MS run. Hence, multiple GC/MS runs may be required to achieve optimum sensitivity for determining tetrachloro through octachloro PCDDs and PCDFs, one for tetrachloro and pentachloro homologs and a second for hexachloro through octachloro homologs. However, the excellent sensitivity of a high performance double focusing (magnetic and electrostatic focusing sectors) mass spectrometer can be sufficient to achieve acceptable detection limits for tetrachloro through octachloro PCDDs and PCDFs in a single GC/MS run, typically significantly lower than possible with a quadrupole spectrometer. A double focusing (magnetic and electrostatic sectors) spectrometer also offers the option of providing additional qualitative verification of PCDDs and PCDFs at higher mass resolutions. However, high resolution mass spectrometry is not typically required for MWC samples.

In many cases, lowest achievable detection limits are requested for PCDDs and PCDFs in MWC stack samples, whether due to very low emission standards and/or very low actual emissions. Hence, high performance magnet mass spectrometers (single or double focusing) are preferred for determining PCDDs and PCDFs in MWC stack emission samples.

3.1.3 Quality Assurance and Quality Control Procedures

3.1.3.1 Calibration of Field Equipment--

Method 5 provides specific procedures for calibrating and leak-checking the sampling equipment. However, additional leak checks should be conducted following each port change.

3.1.3.2 Field Blank Samples--

At least one blank train should be assembled, recovered, and analyzed in the same manner as a sample train for every five tests at each facility. The blank trains should be assembled, leak checked, and the probe and filter box maintained at normal operating temperatures for the duration of a typical test run. However, the sampling pump should not be activated. If a facility test consists of more than five sequential tests, at least one blank train should be run for every five tests.

A complete set of other field blanks should also be taken and reserved for diagnostic analysis if the background contribution from any blank train is unacceptable. These should include at least one from each lot used of the following: sample containers, filters, resin cartridges, and aliquots of rinse solvents.

3.1.3.3 Laboratory Blank Samples--

At least one complete method blank should be analyzed for each lot of samples analyzed and for each extraction/cleanup method combination used. Also, a complete set of laboratory solvents and materials (at least one from each lot used) should be reserved for diagnostic analysis if the background contribution from any method blank is unacceptable.

3.1.3.4 Resin Prescreening--

Each lot of XAD-2 resin should be screened for background contribution prior to use for sample collection. A resin aliquot equivalent to a cartridge charge should be extracted and analyzed in the same manner as a sample, with the exception that extract cleanup can be omitted. If the background contribution is higher than the target quantitation limit for any analyte, that lot of resin should be cleaned by extraction with dichloromethane and a second aliquot screened. Cleaned resin stored for more than 2 weeks should be stored under methanol. The methanol should be removed by decanting and resin dried as described in Method 0010, Appendix B, SW-846. The resin should <u>not</u> be heated.

3.1.3.5 Column Recovery Spikes--

Each lot of samples cleaned by column chromatography should include at least one spiked blank to provide a check on recovery.

3.1.3.6 Relative Response Factor Monitoring--

RRFs for each analyte and MIS compound should be within 20% of the mean RRF for that compound. The RRFs for the daily standards should also fall within 20% of the mean. Alternatively, RRF control charts can be developed and maintained for analyses conducted on a routine basis.

3.1.3.7 Quality Control Check Samples--

A blind quality control check sample should be analyzed with samples from each facility test. The concentrations of native analytes should be in the lower half of the calibration range. The concentrations of MIS and RIS compounds should be the same as in sample extracts. The accuracy results for blind check standard should be within 60 to 120% of the spiked level.

3.1.4 Data Quality Objectives

3.1.4.1 Limit of Detection--

Limits of detection objectives should be based on regulatory requirements. Achieving detection limits significantly lower than regulatory requirements can needlessly increase testing costs. Nonetheless, it is anticipated that very low limits of detection will be required or desired in most cases. Table 3-2 presents target detection limits for PCDDs and PCDFs that are readily achievable using the methods described above with a high performance magnetic focusing GC/MS system. Significantly lower detection limits have been achieved for some MWC tests.

3.1.4.2 Accuracy--

The accuracy objective for blind quality control check sample is 60 to 120% of the spike level. The accuracy objective for recovery of MIS compounds should be 50 to 150%.

TABLE 3-2. EXAMPLE TARGET LIMITS OF DETECTION

Congener	Target detection limit (ng/Nm^3)
TCDD	0.15
TCDF	0.15
PeCDD	0.15
PeCDF	0.15
HxCDD	0.6
HxCDF	0.6
HpCDD	0.6
HpCDF	0.6
OCDD	1.5
OCDF	1.5

3.1.4.3 Precision--

Precision should be evaluated by pooling all the accuracy values, i.e., recoveries, for each MIS compound. For example, the recoveries for the MIS compound $^{13}C_{12}$-2,3,7,8-TCDD should be pooled to determine a single precision value for TCDD determinations. The target for precision is ≤ 50%.

3.1.4.4 Completeness--

The completeness objective for PCDDs and PCDFs in MWC flue gases should be at least 90% valid determinations.

3.2 PARTICULATE MATTER

3.2.1 Method Description

The basic method for measurement of particulate matter in stack gas to determine compliance with emissions limitations or to compare the performance of alternative particulate control devices is that specified in EPA Method 5 (*Code of Federal Regulations*, Title 40, Part 60, Appendix A) and the associated Methods 1-4. This method operationally defines particulate matter as any material that condenses when stack gas is withdrawn isokinetically through a temperature-controlled glass-lined probe and high-efficiency fiber filter.

The Method 5 sampling train is shown schematically in Figure 3-5. The essential elements are a glass- or quartz-lined temperature-controlled probe equipped with a Pitot tube (for measuring stack gas flow rate) and a sharp-edged button-hook nozzle, a glass- or quartz-fiber filter supported in a glass filter holder inside an oven immediately at the outlet of the probe, an impinger train or condenser to remove water, and a pump and metering system.

Procedures for selecting sampling locations and for operation of the train are specified in detail in Method 5 and associated Methods 1 to 4. (Note: EPA has recently relaxed the Method 1 cyclonic flow restrictions for stack sampling. The NESCAUM Work Group has determined that the relaxed restrictions are probably not appropriate for MWC stack sampling and recommends that the more stringent restrictions be maintained for this purpose.) The procedure indicates a sampling rate of 0.5 to 1.0 cubic feet per minute (cfm) or 14 to 28 liters per minute (Lpm) for a minimum of 1 h total sampling time. The minimum total sample size is thus 30 cubic feet (cf) or 1.1 m^3.

3.2.2 Critical Features

3.2.2.1 Sampling Train Hardware--

Hardware suitable for use in EPA Method 5 is commercially available from a number of suppliers and there is no reason to consider a nonstandard train configuration for compliance/performance measurement of particulate matter. Quartz probe liners or water-

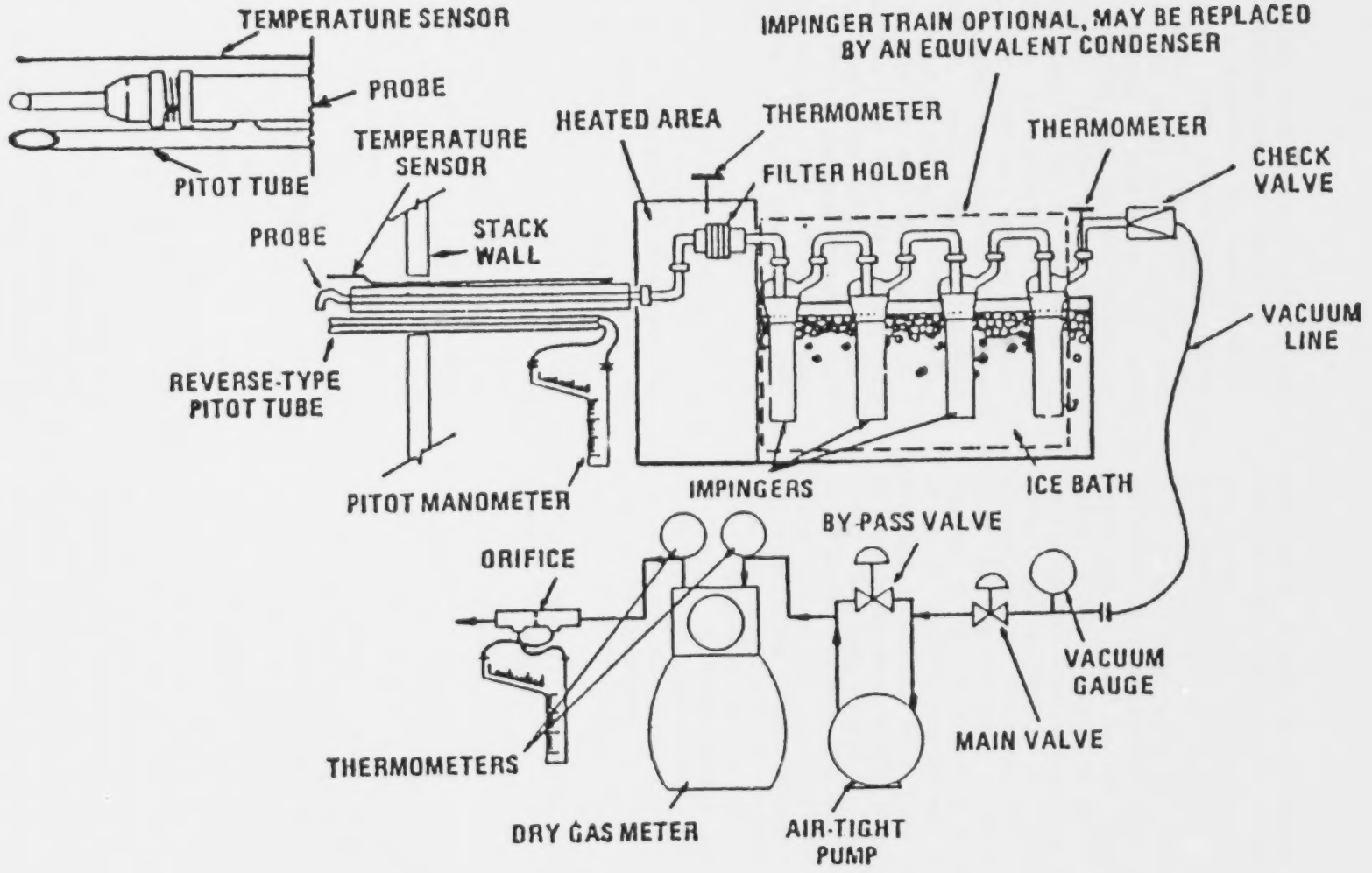

Figure 3-5. Method 5 particulate train. (*Code of Federal Regulations*, Title 40, Part 60, Appendix A)

cooled probes with borosilicate glass liners should be used if the stack temperature is expected to exceed 480°C (900°F). At lower temperatures, borosilicate glass can be used without cooling. The metal probe option allowed in Method 5 should not be used for MWC testing due to the potential for corrosion. If the only purpose for which the sample is to be used is determination of particulate matter emissions, it does not matter whether glass or quartz is chosen as the fiber filter medium. Note, however, that if chemical analysis procedures for, e.g., metals, are to be applied to the collected particulate material after its mass has been gravimetrically determined, the filter medium selected must be shown to be free of analytical interferences and/or background contamination.

3.2.2.2 Sampling Collection Time--

Depending on the particulate material emission standard with which a given facility must comply, it may be necessary to sample for longer than the 1 h indicated in the Method 5 protocol. For example, at an emission rate of 0.010 grains per dry standard cubic feet (gr/dscf), the limit specified in some recent permits, a 2 m^3 or larger sample of stack gas may be required to ensure that the precision of the compliance/performance determination is adequate. The necessary stack gas sample size (and sampling time) for a given test must be calculated by dividing the minimum weighable particulate mass (taking into account the filter tare weight) by the particulate mass emission rate specified in the permit.

3.2.2.3 Hot Zone Sampling--

Some MWC tests may require sampling upstream of air pollution control devices in order to, for example, quantify the removal efficiency achieved by the device(s). The basic method for performing these measurements is the same as described above. However, some additional considerations and method modifications are likely required. The gas flow within the ductwork or breeching from which samples are to be acquired will often not meet the criteria established in EPA Method 1 for Method 5 use. Access to these sampling locations may make traversing the stack cumbersome, at best. If situations are encountered in which exceptions must be made to the Method 5 traversing procedure, it may be possible to perform a velocity traverse and select a point of average velocity, away from the walls of the duct, as a single sampling location. Sampling should be isokinetic at this point. Also, the standard materials for probe construction may not withstand the high temperatures and high corrosivity often present at locations upstream of pollution control devices. At temperatures above 900°C (1650°F), a water-cooled probe jacket is advised. Any exceptions to Method 5 should be approved by the regulatory authority prior to testing.

3.2.3 Quality Assurance and Quality Control Procedures

3.2.3.1 Calibration--

Reference Method 5 specifies in detail the procedures that must be used to calibrate and leak-check the sampling equipment. The analytical balance used for the gravimetric determinations must also be calibrated regularly.

3.2.3.2 Blanks--

Method 5 also specifies that a QC blank sample, consisting of an aliquot of the acetone solvent used for train recovery, be prepared. The Method does not require a blank filter QC sample. However, generation of a field blank filter is standard practice. To ensure comparability with the sample filters,

this blank may be mounted in a filter holder and held at 120° ± 14°C for a time equal to the total sampling run time.

3.2.3.3 Replicates--

It is standard practice to perform Method 5 determinations in triplicate (three separate stack sampling runs).

3.2.3.4 Spikes--

For the particulate matter measurement, the concept of "spiked samples" is not applicable.

3.2.3.5 Calculations--

Method 5 presents the equations to be used to calculate the percent isokineticity and the particulate matter emission rate.

3.2.4 Data Quality Objectives

3.2.4.1 Isokineticity--

Method 5 requires that the isokineticity be in the range of 90 to 110%. Some agencies require that this objective be met for each sampling point, or for specified fraction (percent) of the sampling points, while others require only that the average isokineticity over each run meets the objective.

3.2.4.2 Accuracy--

Method 5 does not include data quality objectives for accuracy of the particulate matter determination.

3.2.4.3 Precision--

Method 5 does not include data quality objectives for precision of replicate determinations. It is usual practice to compute the mean of the three separate determinations and compare this mean value with the emission limitation. Some states, however, require that each of the three measurements fall within the emission limitation.

3.3 METALS

This subsection describes measurement methods for lead (Pb), cadmium (Cd), total chromium (Cr), and mercury (Hg).

3.3.1 Lead, Cadmium, and Total Chromium

3.3.1.1 Method Description--

It is the consensus of the NESCAUM Work Group that EPA Method 12 (*Code of Federal Regulations*, Title 40, Part 60, Appendix A) is the method of choice for compliance testing of lead, cadmium, and total chromium from municipal waste combustors. The basic sampling procedure specified in Method 12 is an EPA Method 5, with 0.1 N nitric acid replacing water in the first two impingers of the train. (See Section 3.2 for description of M5). After sample collection and recovery, the probe wash and impinger solutions are combined and taken to dryness. The residue is combined with the particulate matter on the M5 filter and digested with 50% nitric acid followed by hydrogen peroxide. Lead analysis is by atomic absorption spectroscopy (flame). Cadmium and chromium are determined by atomic absorption spectroscopy (AAS) or inductively coupled plasma (ICP) spectroscopy.

3.3.1.2 Critical Features--

The features of the M5 train discussed in Section 3.2., above, apply to M12 as well.

For determination of lead, cadmium, and chromium it is important that the glass fiber filters used for collection of particulate matter have a lot assay indicating a low background level of the analytes.

It is acceptable to use the same M5 runs for determination both of particulate matter and of cadmium, chromium, and lead. When this option is used, the probe liner should be rinsed with a 0.1 N nitric acid solution after the M5 acetone/water rinses have been performed. This acidic probe rinse is kept separate from the acetone/water rinses and is subsequently combined with the 0.1 N nitric acid impinger solutions, taken to dryness, digested, and analyzed.

The detection limit cited for lead in the method is 0.2 to 0.5 µg Pb/mL of final digested solution. Since the M12 procedure results in a final volume of 250 mL and the standard M5 sample size is 1.1 m^3, the in-stack detection limit for lead is on the order of 45 to 114 µg/m^3. If a lower detection limit is required to determine compliance with permit conditions, three options are readily available:

a. Collection of a larger stack gas sample;

b. Evaporation of the 250 mL digested sample to near dryness and dissolution of the residue in a smaller volume of water; or

c. Substitution of flameless AAS for the flame procedure specified in the method.

The first of these is practically limited to a factor of 2 to 3 improvement in sensitivity (2 to 3 h stack gas sample versus the standard 1 h). With the second, an improvement of a factor of 5 to 10 is probably achievable. A volume smaller than 25 mL may not allow resolubilization of the residue. This alternative also introduces the possibility of some losses through volatilization. Flameless AAS (e.g., SW-846 Method 7421) offers the greatest potential improvement in sensitivity, since inherent detection limits for lead by this technique are about 1,000 times lower than for flame AAS. (SW-846 cites a detection limit of 0.1 µg/L for the furnace Method 7421, versus 0.1 mg/L for the flame AAS Method 7420.) However, the presence of interferences may limit the sensitivity improvement achievable on actual samples to less than 1,000-fold.

The detection limits for cadmium and chromium in the solution analyzed by the ICP method are about 4 µg/L and 7 µg/L, respectively. For a standard 1.1 m^3 M5 sample, and a final extract volume of 250 mL (as specified in M12), these correspond to in-stack detection limits of 1 µg/m^3 for cadmium and 1.8 µg/m^3 for chromium. If flame AAS is used for the determination, the detection limits increase to 1.3 and 11 µg/m^3.

If lower detection limits are required for cadmium or chromium, the options are essentially the same as described under lead, above. The simplest option is to reduce the volume used in diluting the sample after digestion. Depending on sample characteristics, however, a final sample volume of less than 25 mL is probably not practical. On the other hand, if flameless (graphite furnace) AAS is used as the analytical technique, inherent detection limits are considerably lower: 0.01 µg/m^3 for cadmium and 0.1 µg/m^3 for chromium. Keep in mind that interferences (e.g., iron) may raise these detection limits somewhat for real samples.

3.3.1.3 Quality Assurance and Quality Control Procedures

Calibration. The sampling equipment must be calibrated as specified in M5. Laboratory balances must be calibrated according to a regular schedule. The AAS system is calibrated for wavelength accuracy according to the manufacturer's specifications.

M12 specifies that the quantification be accomplished by reference to a six-point external standard curve covering the range of 0 to 20 µg/mL of lead. Samples must be diluted as necessary to fall within the calibration curve range. The method specifies that the curve is not to be force-fit through zero. The same procedures should be used in generating standard curves for cadmium and chromium.

It is acceptable to prepare a single set of calibration standards containing cadmium, chromium, and lead, depending on the determinative technique(s) chosen for the analysis. An HCl solution is required when the analysis is to be done by ICP or flame AAS, nitric acid is used for furnace AAS.

Blanks. M12 specifies that a filter blank be created using two filters from each lot used in the sampling train. The filter blank sample is digested in the same fashion as the samples, however, the method specifies that the blank be made to a final volume of only 100 mL.

The method also specifies that a 0.1 N nitric acid blank be prepared by taking 200 mL of solution to dryness and digesting the residue as if it were a sample. Again the final volume is made to 100 mL.

The method states that the absorbance readings for samples are to be corrected for both the filter blank and the nitric acid blank absorbances.

Replicates. Samples, filter blanks, and nitric acids blanks are analyzed in triplicate. The mean of the three determinations is used to read the sample concentration from the standard curve.

It is common practice to base compliance determinations on the mean of the lead emissions as measured in three separate stack sampling runs.

Spikes. The method requires that at least one sample from each source tested shall be analyzed by the method of additions as a check on possible matrix effects. One aliquot of the sample is analyzed unspiked and a second aliquot is mixed with an equal volume of standard solution. The concentration of the analyte in the sample solution, C_s, is calculated as:

$$C_s = C_a \times \frac{A_s}{A_t - A_s}, \text{ where}$$

C_a = Analyte concentration in the standard solution
A_s = Absorbance of the unspiked sample solution
A_t = Absorbance of the spiked sample solution

Calculations. M12 presents the equation for calculating the stack gas concentration of lead in milligrams per cubic meter (mg/m^3). Analogous equations should be used to calculate stack gas concentrations for cadmium and chromium.

3.3.1.4 Data Quality Objectives--

Calibration Curve. No numerical data quality objectives are established for acceptance of the standard curve (e.g. correlation coefficient). However, the method implies that a y-intercept value exceeding 0.003 absorbance units indicates a potential problem with standard solution preparation or nonlinearity of the standard curve.

Accuracy. The data quality objective (DQO) is that C_s calculated as shown above from the spiked and unspiked sample absorbances be within 5% of the value obtained by reading the sample concentration directly from the calibration curve. This is equivalent to an accuracy goal of 95 to 105% recovery for each spiked analyte. If DQOs are not met, all samples must be analyzed by the method of additions.

Precision. No numerical data quality objectives for precision of the replicate measurements on samples or blanks is stated. However, M12 states that calibration standard analyses shall be repeated until two consecutive absorbance readings agree within 3%.

3.3.2 Mercury

3.3.2.1 Method Description--

It is the consensus of the NESCAUM Work Group that EPA Method 101A (*Code of Federal Regulations*, Title 40, Part 61, Appendix A) is the method of choice for compliance testing of mercury emissions in MWC stack gas.

Method 101A collects mercury in impingers containing acidic potassium permanganate solution. The basic sampling method is EPA Method 5. However, the use of a filter is optional in the train for the M101A determination. The filter may be required when sampling streams with high particulate loadings, as in locations upstream of air pollution control devices. The probe wash solution specified in the method is 250 to 400 mL of fresh 4% $KMnO_4$ solution. After sample collection and recovery, the probe wash and impinger solutions are combined. If a filter was used in the train, it is added to the acidic permanganate solution. This is taken to near dryness and then digested with concentrated nitric acid. The digested solution is combined with the impinger solutions and the filter discarded. The combined solutions are diluted in an acidic aqueous medium, the mercury is reduced to elemental form, and determined by cold vapor AAS.

3.3.2.2 Critical Features--

The critical features of the M5 train discussed in Section 3.2, apply to M101 as well. For mercury determination, it is important to ensure that the collecting medium (acidic permanganate solution) does not come into contact with any greased surfaces. It is also necessary to avoid the use of metal probe liners. Borosilicate glass or quartz are acceptable.

A minimum stack gas sampling period of 2 h (versus 1 h for standard M5) is recommended. However, the method notes that high organic material concentrations may cause the collection medium to become exhausted (bleaching of purple permanganate color) before the 2 h sampling is completed. If the impinger reagents have no perceptible purple color at the completion of the run, the sample should be considered invalid and the run repeated. To avoid the need for resampling, the sampling crew is advised to monitor the reagent color throughout the run and to replace the reagents with fresh solution if significant fading is observed. The impinger reagents would then be combined prior to analysis.

The detection limit for mercury analysis by cold vapor techniques is about 0.2 µg/L in the solution as analyzed. Using the standard dilutions specified in M101A (probe wash and impinger solutions made to 1 L, then diluted 2 to 250 mL), this corresponds to an in-stack detection limit of 11 µg/m³ for the recommended 2 h (2.2 m³) sample. If a lower detection limit is required two options are readily available:

a. Collection of a larger stack gas sample, or

b. Use of a smaller secondary dilution factor.

The first option may be limited because of the relatively low capacity of the permanganate collection reagent, especially in sources emitting significant quantities of organic material. The second option is probably capable of achieving a factor of 10 improvement in sensitivity.

3.3.2.3 Quality Assurance and Quality Control Procedures

Calibration. The sampling equipment must be calibrated as specified in M5. Laboratory balances must be calibrated according to a regular schedule. The AAS system is calibrated for wavelength accuracy according to the manufacturer's specifications.

M101A specifies that quantification be accomplished by reference to a six-point external calibration curve, covering the range of 0 to 1,000 ng of mercury per analysis. The calibration curve is not force-fit to zero.

Blanks. Method 101A specifies that blank determinations be performed on the collection medium and on the filter (if used). In addition, a blank corresponding to the 0 mg/L calibration standard should be rerun after every five samples. The standard and sample data are blank corrected.

Replicates. The method requires that replicate aliquots of diluted samples and of calibration standards be analyzed until two consecutive peaks agree within the data quality objective (see below.) It is the mean of the two values that is used to build the calibration curve (standards) or calculate concentrations (samples). Method 101A requires that compliance determinations be based on the mean of the mercury emissions as measured in three separate stack sampling runs.

Spikes. M101A does not require the analysis of spiked samples. However, it does recommend that at least one sample from each stack test be checked by the method of standard additions. The NESCAUM Work Group recommends this procedure for MWC tests.

Calculations. M101A presents the equations for calculating the total mercury in the sample (µg) and the emission rate in grams per day (g/day). The NESCAUM Work Group recommends that mercury results also be reported in concentration units (µg/m^3).

3.3.2.4 Data Quality Objectives--

Isokineticity. The isokinetic variance and acceptance criteria are the same as for M5.

Calibration curve. The method does not specify a goodness-of-fit data quality objective (e.g., correlation coefficient) for the calibration curve. It does specify that the y-intercept for the curve should not exceed a value corresponding to 2% of full scale.

Accuracy. There is no numerical data quality objective for accuracy (recovery) for this method.

Precision. The numerical data quality objective for precision is that the peak height (or area) measured for successive analyses of the same sample or standard agree within 3%. There is no numerical data quality objective for reproducibility of results for the triplicate stack sampling runs.

3.4 COMBUSTION GASES--CARBON MONOXIDE, CARBON DIOXIDE, AND OXYGEN

3.4.1 Method Description

The consensus method for determination of carbon monoxide and carbon dioxide is the use of instrumental monitors based on the principle of non-dispersive infrared spectroscopy.

For carbon monoxide, this is equivalent to the instrumental version of EPA Method 10. Although Method 10 has not been validated by EPA for the MWC source category, its use is generally accepted by state regulatory authorities. EPA Method 3 (Orsat) is an acceptable alternative to instrumental methods for CO, O_2, and CO_2. In

Method 10, a sample of stack gas is withdrawn through a stainless steel or sheathed Pyrex glass probe equipped with a filter to remove particulate matter, a condenser and/or silica gel trap to remove excess moisture, and an ascarite trap to remove CO_2, then introduced into the NDIR analyzer. There is no requirement for traversing the stack or for maintaining isokinetic sampling conditions; the sample is obtained from the midpoint of the stack or from another convenient location at least 3.3 ft from the stack wall.

For carbon dioxide, the equivalent method is EPA Method 3A, using an NDIR instrument for the CO_2 determination. The probe, filter, and condenser/silica gel trap are as in EPA M10. However, the ascarite tube is not included in the train. In this method, it is specified that a minimum of 8 to 12 traverse points be sampled.

For oxygen, the recommended method is instrumental monitoring using a paramagnetic or polarographic analyzer. The reference method is 3A. As described above for CO and CO_2 determinations, a gas conditioning system for removal of particulate matter and excess moisture must be included upstream of the instrumental analyzer.

3.4.2 Critical Features

Housing the analyzers in a clean, thermally stable, vibration-free environment will minimize instrument drift.

When the CO concentration in the stack or flue gas is low (i.e., less than 50 ppm), some field investigators have found that varying (%) levels of CO_2 may cause interferences in the CO determination. The use of an NDIR instrument equipped with a gas filter correlation system will minimize these effects. As an alternative, the NDIR instrument can be calibrated with gas mixtures containing CO in CO_2 at the levels expected in the gas stream.

If the MWC is not equipped with a system for acid gas removal, there is potential for corrosion of optical components within the NDIR instruments. However, most HCl will be removed from the gas stream in the condenser.

3.4.3 Quality Assurance and Quality Control Procedures

The methods specify the use of calibration gases for performance testing of the NDIR instruments. A minimum of three gas mixtures - one high, one mid-range, and one zero - are to be used. For CO analysis the gas mixtures should be CO in nitrogen. (Note that in calculating the CO concentration in the stack gas, a correction must be made for the volume of CO_2 removed by the ascarite gas conditioner.) For CO_2, mixtures in nitrogen, air, or $O_2/CO_2/SO_2$ matrices may be used. For CO_2, the method specifies that system bias be checked by introducing the calibration gases at the outlet of the probe, upstream of the sample conditioning system (condenser and, for CO analysis, ascarite removal tube). Certified gas mixtures, traceable to the National Bureau of Standards should be used for bias checks.

Since the instrumental methods recommended here are accepted EPA procedures, it is not necessary to perform confirmatory testing by manual procedures each time the measurements are made. However, if instrument problems are observed, or if the response to calibration gas mixtures is nonreproducible, manual checks may be advisable. For CO_2 and O_2 determinations, Orsat measurement can be made in parallel with the instrumental determinations. Method 3A cross references Method 6C (instrumental determination of sulfur dioxide emissions) for specification of calibration error, sampling

system bias, zero drift, calibration drift, and interference check determinations.

3.4.4 Data Quality Objectives

Method 10 does not set numerical data quality objectives for CO determination. However, it states that the precision of most NDIR analyzers is approximately 2% of full span and the accuracy about 5% of full scan.

For CO_2 determinations, Method 3A, by reference to Method 6C, sets data quality objectives as follows: analyzer calibration error less than 2% of span for zero, mid-range, and high calibration points; sampling system bias less than 5% of span for zero, mid-range, and high calibration mixtures; zero drift less than 3% over the period of each run; calibration drift less than 3% over the period of each run; and interference check less than 7% of the CO_2 concentration observed in each run. Method 3A also specifies that differences between the Orsat and instrumental results greater than 0.5% CO_2 should be investigated. Possible sources of discrepancies are leaks in the sampling system, inadequate moisture removal, or fouling of the optical components in the instrument. Sampling should not be continued until the source of the problem has been found and corrected.

The data quality objectives for oxygen determination are the same as those specified above for CO_2 under Method 3A. However, in the case of oxygen there is no numerical objective for agreement between the Orsat and instrumental measurements.

Equations for calculating the stack gas concentrations are given the the respective methods.

3.5 TOTAL HYDROCARBONS (THC)

3.5.1 Method Description

The NESCAUM Work Group recommends the use of EPA Method 25A for determination of THC in MWC emissions. In this method (*Code of Federal Regulations*, Title 40, Part 60, Appendix A), a gas sample is extracted through a stainless steel rake type probe, heated gas sample line, and glass fiber filter to a flame ionization detector (FID).

3.5.2 Critical Features

The FID is calibrated using propane (or other alkane) in nitrogen. The results may be reported as ppm carbon, ppm as methane, ppm as propane, etc. However, the basis of the reporting method must be stated.

In Method 25A, the FID is operated as if it were a total hydrocarbon analyzer. This is, of course, only an approximation since different organic compounds have different FID response factors. Highly oxygenated or halogenated organics, for example, have relatively weak FID responses. However, the FID is as close to being a "universal" hydrocarbon detector for field use at ppm levels as any device currently available. If the parameter of concern is nonmethane total hydrocarbons (NMTHC), the measurement can be made both with and without a carbon filter in place upstream of the analyzer. The difference between the total and the filtered gas stream measurements will provide a measure of NMTHC. An alternative approach is to incorporate a gas chromatographic (GC) separation prior to FID detection. This can provide at least tentative identification of the types (boiling point distribution and possibly specific compound assignments based on retention times) of hydrocarbons present in the gas stream.

EPA Method 25 is a possible alternative to Method 25A. However, Work Group members report that Method 25 is subject to interferences from the high levels of CO_2 and water present in MWC combustor effluents, and may give erroneously high results. The Work Group thus recommends Method 25A, although some agencies still require that Method 25 be used to determine compliance.

Acceptability of the proposed THC method should be confirmed with the appropriate regulatory agency(ies) prior to testing.

3.5.3 Quality Assurance and Quality Control Procedures

Calibration. Method 25A requires that the FID response range be defined using zero gas and a span gas containing 1.5 to 2.5 times the expected THC level. A three point calibration curve is then constructed for quantification.

Replicates. The method provides no specific guidance on the number of replicate measurements or the averaging time to be used in determining compliance with permit emission limitations. These must be established in discussions with regulatory authorities for each test.

3.5.4 Data Quality Objectives

The method specifies that zero drift and span drift over the duration of a series of measurements must be no more than 3%. Also, the calibration error shall be less than 5% of the calibration gas value.

3.6 OTHER GASES

The other gases the NESCAUM Work Group members consider to be of potential concern in most MWC compliance testing are the acid gases: NO_x, SO_2 as an indicator of sulfur oxides, and hydrochloric acid (HCl). Methods for the first two of these acid gas parameters are well developed. Methods for measurement of HCl in MWC emissions have been less widely used although validation has not been completed. This is particularly true of methods for continuous monitoring of HCl, which are still in a method development stage.

3.6.1 Hydrochloric Acid

3.6.1.1 Method Description--

The NESCAUM Work Group agreed that HCl should be collected in the impinger portion of the M5 train. After sample collection and recovery according to M5 procedures, the impinger solutions are combined and made to a convenient volume (e.g., 1 L) for analysis. The pH is adjusted as necessary to accommodate the analytical finish. The Cl^- ion concentration in the resulting solution is determined by ion chromatography, specific ion electrode, or titration against standard silver nitrate or mercuric nitrate (e.g., SW-846 Method 9252).

3.6.1.2 Critical Features--

There is a lack of consensus on the impinger reagent most appropriate for collection of HCl from MWC stack gas. The use of 0.1 N NaOH is frequently specified. Some Work Group members recommend use of a sodium carbonate solution, since this reagent will not absorb CO_2. There is evidence to suggest that caustic reagent is not necessary, and that HCl is efficiently trapped in any aqueous medium. If this is true, then distilled water (e.g., ASTM Type II reagent water) will be the reagent of choice for collection of HCl.

The features of the M5 train discussed in Section 3.2 above, apply to HCl sampling as well. It is acceptable

to perform the HCl determination on the back half of the train used for particulate matter determination. It has also been suggested (EPA Environmental Monitoring Systems Laboratory, Research Triangle Park, North Carolina) that HCl collection can be incorporated into a multiple metals sampling train. However, a train containing both basic impingers for HCl and acidic impingers for metals has not yet been tested. If such a train were used, it would be necessary to ensure that all impinger solutions are representatively tested for all species of concern. If an M5-type train is to be used only for HCl determinations, it is not necessary to sample isokinetically.

The detection limit for HCl will depend on the detection limit of the analytical technique chosen. Using SW-846 Method 9252, the detection limit in the solution as analyzed is less than 2.5 mg/L. For a standard M5 stack gas volume of 1.1 m^3, assuming a final impinger solution volume of 1 L, this corresponds to an in-stack detection limit of about 2.3 mg/m^3. The detection limits of the ion chromatography and specific ion electrode determination methods are typically less than 1 mg/L. Many samples may require dilution to fall within the linear range of the Cl^- determination method, especially for samples collected upstream of the acid gas removal system (or at older facilities with no acid gas removal system in place).

3.6.1.3 Quality Assurance and Quality Control--

The quality control procedures recommended in SW-846 Method 9252 are applicable to each of the methods described above. These include:

Blanks. A minimum of one blank per sample batch. The blank should consist of a volume of 1 M NaOH equal to that charged to the M5 impingers.

Replicates. A minimum of one duplicate sample for every 10 field samples.

Spikes. Spiked samples or standard reference materials should be analyzed "periodically."

3.6.1.4 Data Quality Objectives--

Numerical data quality objectives have not been established for the determination of HCl in MWC effluents. It is expected that a precision corresponding to better than 3% CV and an accuracy of better than 5% should be achievable by the specified analytical methods at HCl emission levels of 50 ppm or higher. The uncertainty introduced by sampling variations cannot be assessed at this time.

3.6.2 Nitrogen Oxides

3.6.2.1 Method Description--

The NESCAUM Work Group recommends EPA Method 7E as the basic procedure for compliance testing of MSW combustors for NO_x emissions. In this method a sample is withdrawn continuously and conveyed to an instrumental chemiluminescent analyzer for determination of NO_x concentration. The Work Group also considers EPA Method 7A an acceptable alternative. In this method, a grab sample of stack gas is collected in an evacuated flask containing a diluted sulfuric acid/hydrogen peroxide absorbing solution. The nitrogen oxide emissions, except nitrous oxide, are oxidized to nitrate and determined by ion chromatography.

In both methods, the sample interface consists of a borosilicate glass, stainless steel, or Teflon probe equipped with a filter (glass wool plug) to remove particulate matter. Selection of sampling locations is cross referenced to EPA Method 7.

3.6.2.2 Critical Features--

Method 7A is specific for NO_x species other than nitrous oxide. The instrumental analyzer used in Method 7E is based on detection of NO_x as NO and incorporates a converter to reduce any NO_2 present to NO prior to quantification. It is critical that the converter efficiency be checked prior to each test. It is also critical that an acceptable water removal mechanism be incorporated into the sample conditioning system.

The grab sampling method, 7A, gives only a snapshot indication of the NO_x emissions. A number of replicate determinations (minimum three per test) are needed to ensure that the results are representative of source emissions. The number of replicates and the required averaging time for NO_x emissions should be confirmed with the regulatory agency(ies) for each MWC test.

Particulate plugging problems may be expected when applying either of these methods upstream of air pollution control devices.

3.6.2.3 Quality Assurance and Quality Control Procedures--

Stack sampling equipment and laboratory instrumentation are to be calibrated as stated in the methods or manufacturer's specifications.

If available, audit samples should be analyzed. Audit gas samples are provided by the U.S. Environmental Protection Agency's Environmental Monitoring Support Laboratory (Research Triangle Park, North Carolina).

Method 7A requires the generation of a five-point calibration curve for quantification. Method 7E requires the use of three calibration gases consisting of NO in nitrogen at high, mid-range, and zero concentration levels.

Neither method explicitly requires a blank determination and requirements for replicate sample determinations are not stated.

3.6.2.4 Data Quality Objectives--

Both Method 7A and Method 7C require that the results of the QA audit sample analysis be within 10% of the actual audit concentrations. Method 7A also requires that the calibration curve be sufficiently linear than none of the five calibration points deviates from the linear regression line by more than 7% of the concentration at that point. Method 7E requires conformance to the data quality objectives stated in Method 6C for analyzer calibration error and sample system bias. Neither method present numerical data quality objectives for precision and accuracy of sample measurements.

3.6.3 Sulfur Dioxide

3.6.3.1 Method Description--

The NESCAUM Work Group preferred method for compliance testing measurement of sulfur dioxide is EPA Method 6. The basic sampling train specified in this method consists of: a borosilicate glass or stainless steel probe with a quartz or pyrex wool plug for particulate removal; a midget bubbler containing isopropyl alcohol for absorption of SO_3; and midget impingers containing hydrogen peroxide solution for collection of SO_2; plus the usual valves and metering system. The method also allows the options of sampling SO_2 in an M5 train, with hydrogen peroxide replacing water in the impingers, or a Method 8 train (like M5 but with an unheated filter placed between the first two impingers), with isopropyl alcohol in the first impinger and hydrogen peroxide in the back-up impingers. After sample collection and recovery, the contents of the hydrogen peroxide impingers are combined and

made to volume with distilled water. The SO_2 is determined by as sulfate ion by titration with barium perchlorate to a Thorin endpoint or by ion chromatography. An acceptable alternative is Method 6C, based on an instrumental analyzer.

3.6.3.2 Critical Features--

Free ammonia is a known interference in Method 6. This could be a problem when testing at an MWC that uses post-combustion NO_x control techniques, such as Selective Catalytic Reduction (SCR).

The midget bubbler containing the isopropyl alcohol for SO_3 removal must be packed with glass wool at the top to prevent carry-over of sulfuric acid mist.

When sampling in locations upstream of particulate matter control devices, it may be necessary to use a high efficiency glass fiber filter in place of the glass wool plug. High concentrations of cations generated by collection of fine metal fumes in the hydrogen peroxide impingers would interfere in the analysis.

Method 6 sets no specific criteria for selection of sampling sites. It is recommended that sampling be performed at a point of average velocity near the center of the stack/duct, at least 3 ft away from the stack wall. Isokinetic sampling is not required.

The detection limit of Method 6 has been determined to be 3.4 mg/m^3 of SO_2. The upper limit of the method is about 93,000 mg/m^3 for a 20 L sample of stack gas.

When the instrumental analyzer Method 6C is used, it is necessary to check the instrument performance using Method 6 as a reference method.

3.6.3.3 Quality Assurance and Quality Control Procedures--

Calibration. Sampling equipment must be calibrated and leak-checked as described in the method. Laboratory equipment, including balances, must be calibrated on a regular schedule in accordance with manufacturers' specifications.

The collection efficiency of the sampling train must be determined by performing at least three tests with a fourth hydrogen peroxide impinger in the train. The contents of the fourth impinger are analyzed separately.

The titrimetric quantitative analysis technique is calibrated by titration of sulfuric acid solutions that have been standardized against 0.0100 N NaOH, which has been standardized against primary standard grade potassium acid phthalate.

Blanks. The method requires the analysis of a blank with each series of samples.

Replicates. The method requires that each sample be analyzed in duplicate.

Audit samples. If available, audit gas samples should be analyzed. Audit gas samples are provided by the U.S. Environmental Protection Agency's Environmental Monitoring Support Laboratory (Research Triangle Park, North Carolina).

3.6.3.4 Data Quality Objectives--

Precision. Replicate titrations must agree within 1% or 0.2 mL, whichever is larger.

Accuracy. Numerical criteria for equipment calibration and leak checks are given in the method.

The results of analyses of the QA audit samples must agree to within 5% of the known value.

The collection efficiency must be at least 99% for a series of three tests. This requires that the sulfate content of the fourth impinger not exceed 1% of the total sulfate recovered from the first three impingers.

SECTION 4.0

RESULTS REPORTING

4.1 OVERVIEW

The NESCAUM Work Group agreed that the reporting of results of MWC testing, whether for compliance, performance, or research and development, should use a format that meets the following criteria:

- Allows the reader to readily determine what the test objectives were and whether they were met,
- Expresses all data for compliance testing in the units specified in the permit and/or regulation,
- Provides an indication of the data quality in terms of range, standard deviation, or error bounds, and compares the actual data quality indicators with the data quality objectives set for the tests,
- Cross-references summary data to more complete back-up information, which may be in appendices, and
- To the extent possible, meets the needs of multiple potential users: permitters/regulators, legislators, air quality modelers, risk assessors/toxicologists, data base builders.

The Work Group felt that it would not be burdensome to require that results be reported in a consistent format for all tests. It was recognized that this might require reporting some results in two different forms--once in the compliance units and once in the NESCAUM common format.

The group developed a list of auxiliary parameters to be reported. Along with basic process operating data are included the information needed to convert the data from the NESCAUM common units to units appropriate for other specific uses, e.g., allow easy conversion from stack concentration in $\mu g/m^3$ to emission rate in grams per second (g/sec) or emission factor in pounds per ton (lb/ton) of refuse. The Work Group recognizes that some of the process operating data may not be readily available for all tests. For example, MWC facilities will usually not have measurements of the heat content of the refuse in Btu/lb, although they may have estimates based on the calorimetric performance of the combustor. To the extent possible, estimated values of nonmeasured parameters should be reported, along with an indication of the method used to develop the estimate. The Work Group recommends that this list of auxiliary parameters to be reported should be used as a checklist by the field testing crew to ensure that as much as possible of the potentially useful information is recorded for each unit tested.

4.2 RESULTS TO BE REPORTED

4.2.1 Facility Operating Status

The Work Group decided that the following process data should be included in the body of an MWC stack test report:

- Feedrate of waste expressed as: (1) the rate of steam production,

(2) the percentage of the design capacity steam production, (3) the average measured or calculated mass loading of waste (tons/hour [T/h] or tons/day [T/day], and (4) the heating value of the waste in Btu/lb (measured, estimated, or assumed for purposes of calculating feedrate).

- All available data concerning the composition and source of refuse (e.g., % moisture, % ash, % residential, etc.).

- Combustion temperature(s) supported by a schematic drawing indicating the measurement location(s), specification of the device(s) used for temperature measurement, and an indication of how the devices were shielded, etc. (Note: Measurement of combustion temperatures is still an inexact science. Meaningful comparisons between facilities cannot be drawn unless this supporting information is reported.)

- Pressure drop across the boiler.

- Percent excess air.

- Air pollution control device parameters (such as ESP electrical data).

- If a soot blowing episode(s) was included in the sampling period, its duration.

- Facility status prior to test, i.e., "cold" start or continuing operation.

The Work Group also agreed that most other ancillary process data that were recorded by the tester or by the facility during the testing period should be included in appendices to the report. It is felt that this represents an important opportunity to document an operational baseline for the facility during a time when its emission status was established. These results would be potentially useful to owner/operators or regulators in trouble-shooting problems that might arise in the future. Table 4-1 presents a list of facility operating data that should be recorded for each test run.

4.2.2 Combustion Process Data

The report should include, in tabular format, a summary of data relating to the overall combustion and air pollution control device performance. This would include, for each test run:

Stack temperature
Stack gas % moisture
% Isokineticity
Stack gas flow rate (m^3/sec)
Concentrations of combustion gases and acid gases
Particulate loading

4.2.3 Permit Conditions

The Work Group believes it would be helpful to the MWC test report reader to have a tabular summary of the emission limitations (if applicable) imposed on the facility as permit conditions in the body of the report. Table 4-2 is a pro forma table for listing permit conditions.

4.2.4 Pollutant Emission Data

For each pollutant tested, the report should show, in tabular form, the value measured for each run as well as the mean of the three (or more) replicate stack tests. It was felt that a table showing only the mean value would not convey sufficient information concerning the uncertainty of the results. This could result in misuse of the data for comparative purposes.

The Work Group consensus is that metric units should be used consistently in the reporting of MWC emission data. For organic and inorganic chemical pollutants, the Work

TABLE 4-1. MWC FACILITY OPERATING DATA

1. Boiler/Furnace Data

Steam flow (lb/h) set point and actual
Superheater outlet temperature (°F)
Superheater outlet pressure (psi)
Feedwater flow (lb/h)
Feedwater temperature (°F)

Combustion air temperature (°F)
Furnace draft (in. H_2O)
Total combustion airflow (acfm)
Secondary air pressure(s) (in H_2O)
Furnace temperature(s) (°F)
Economizer exit gas temperature (°F)
Excess Air (%)
CO and O_2 (ppmv and %)
Sootblowing (frequency and duration)

2. Electrostatic Precipitator Operating Data

Secondary field current (mA) for each field
Secondary field voltage (KV) for each field
Rapping cycle (frequency and duration)

3. Acid Gas Absorber Operating Data

Inlet temperature (°F)
Outlet temperature (°F)
Wet: Slurry concentration (% or specific gravity)
Slurry feedrate (gpm)
Dilution water flow rate (gpm)
Atomizing air pressure (psi)
Control mode - automatic/manual
Dry: Lime injection rate (lb/h)

4. Baghouse Operating Data

Iniet temperature (°F)
Outlet temperature (°F)
Pressure drop (in. H_2O)
Cleaning cycle control - automatic/manual
Cleaning cycle - pressure drop versus timed cycle
Cleaning cycle - frequency and duration

TABLE 4-2. PRO FORMA TABLE FOR REPORTING PERMIT CONDITIONS AND TEST RESULTS

Parameter	Units	Permit limitation	Averaging time	Test results	Comment/reference
Process parameters					
Furnace temperature					
Refuse feedrate					
Other (e.g., combustion efficiency:					
Stack emissions					
Particulates					
CO					
2,3,7,8-TCDD equivalents[a]					
Lead					
Mercury					
Cadmium					
Chromium					
HCl					
NO_x					
SO_2					
Others:					

[a] Citation for equivalents calculation.

Group agreed that the appropriate unit for reporting in the common NESCAUM format should be µg/Nm³ or ng/Nm³. Normal conditions are defined as: dry, 0°C, and 1 atm corrected to 7% O_2. The correction factor (CF) for 7% O_2 is:

$$CF = \frac{14}{20.9-Y}$$

where Y is the volumetric oxygen percentage measured in the stack.

The Work Group actively considered both 12% CO_2 and 7% O_2 as the basis for normalizing concentrations. Although some permit conditions [e.g., particulate matter emission limitations] continue to be written on a 12% CO_2 basis, the Work Group finally chose 7% O_2 as its recommended normalizing factor. One reason cited for this selection was that it obviates the need to specify whether CO_2 produced by combustion of auxiliary fuel should "count" in the correction factor. On the other hand, the use of the 7% O_2 basis is complicated by possible in-leakage of air between the combustion zone and the measurement location. In the end, the Work Group recognized that this choice was somewhat arbitrary and that neither basis was strongly preferable to the other on technical grounds. The Group did feel strongly that a single consistent method of correcting the data should be adopted.)

Some state agencies also require that uncorrected data be reported. If this is a requirement, the Work Group recommends that the raw (uncorrected) data be included in an appendix to the report of test results.

Gaseous species (O_2, CO_2, CO, HCl, SO_x, and NO_x) are exceptions to this general rule and should be reported in concentration units of percent or parts per million volume (ppmv) corrected to standard conditions of: dry, 68°F, 1 atm, and 7% O_2.

In the NESCAUM consensus format, particulate matter should be reported in milligrams per cubic meter (mg/Nm³) at the same standard conditions. If the emission limitation specified by the regulation/permit is simply comparable to the reported emission concentrations for a particular pollutant, the group felt that the emission limit should also be included in the summary table.

4.2.5 Conversion Factors

As noted above, the Work Group felt that units reflecting mass of pollutant (or volume for gases) per volume of stack gas is the most generally useful format for many purposes. However, it was recognized that other reporting bases are more convenient for many purposes. Other types of units in common use include:

- mass/time (e.g., g/sec)
- mass/mass of refuse (e.g., lb/ton)
- mass/HHV (e.g., lb/10^6 Btu)
- mass/mass of stack gas (e.g., lb/1,000 lb flue gas)

To accommodate users who wish to convert the mass/volume concentration units into one of these alternative bases, the data shown in Table 4-3 should be included in the report. Table 4-3 lists only the facility-specific information that is required for the conversions. Factors for converting between English and metric units or from nanogram to gram (ng to g) can be included in an appendix to the test results report. Table 4-3 also includes the heating value of the refuse (Btu/ton) as one of the test conditions to be reported. The "comment/reference" column of the table should indicate the basis for the reported value (e.g., direct measurement, calculated from steam production, etc.).

TABLE 4-3. PRO FORMA TABLE FOR TEST CONDITIONS DATA

Parameter	Unit	Run 1	Run 2	Run 3	Mean	RDP*	Comment/reference
Operating conditions							
Refuse Feedrate*	T/day						
Heat content* (as received)	Btu/lb						
Moisture*	%						
Total ash*	%						
Steam flow rate	lb/h						
Heat absorbed by boiler	Btu/h						
Boiler efficiency	% of heat release						
Stack gas parameters							
Flow rate	Nm^3/s dscf/min dscf/Btu lb/h (dry)						
Temperature	°F						
Moisture	%						
Test time	24 h clock						

* Indicates basis for estimate.

4.3 DATA TABULATION FORMATS

Tables 4-4 through 4-7 present pro forma tables for data reporting. The NESCAUM Work Group feels strongly that all data should be presented with an appropriate indication of its reliability. This is accomplished, in part, by indicating the individual measurements, as well as the mean, in all data tables. In addition, the group recommends that any measurement not meeting the relevant data quality objectives (precision, accuracy, recovery of spiked material, etc.) should be reported conditionally (e.g., asterisk to an explaining footnote).

4.4 DATA QUALITY RESULTS REPORTING

Table 4-8 presents a suggested format for reporting data quality results and for comparing them with data quality objectives. For purposes of illustration, only the PCDD/PCDF data quality results are shown in the pro forma table. For an actual test, comparable results should be reported for each indicator of DQO attainment for each parameter tested.

4.5 REPORTING "NOT DETECTED" VALUES

In an ideal world, the issue of reporting "not detected" (ND) results would be a moot point, because the sampling and analysis methods used would have detection limits so far below the level of possible concern that an ND was functionally equivalent to zero. Unfortunately, especially in the case of PCDD/PCDF and some trace metals, the analytical detection limit and the lower level of concern (or emission limitation) are essentially the same (to within an order of magnitude). This creates a temptation to assign a concentration to ND values equivalent to the detection limit or some fraction of the detection limit. When the emission limitation applies to the sum of concentrations of a number of related pollutants (e.g. PCDD/PCDF or PCBs) the assignment of finite numerical concentrations to a series of ND results can easily give rise to false positive results.

ND values should not be assigned finite concentration values for summation purposes. The ND values should be reported as such in the data summary tables, with the detection limit of the method for that sample shown in parenthesis, e.g.,

2,3,7,8-PeCDD ND (7 ng/Nm^3)

If other PCDDs above the detection limit had been found in the sample, the total PCDD concentration would be reported as the sum of the apparent positive findings, but would not include a 7 ng/m^3 contribution from P_5CDD. If no PCDD had been found in the sample, the total would be reported as ND. However, in this case the number in parentheses probably should be the sum of the detection limits.

SECTION 5.0

CITED REFERENCES

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TABLE 4-4 PRO FORMA TABLE FOR CONVENTIONAL EMISSION PARAMETER

Parameter	Unit	Run 1	Run 2	Run 3	Mean	RPD	Comment/reference
Stack gas flow rate	dscf/s						
Stack gas velocity	ft/s m/s						
Stack temperature	°F						
Stack gas moisture	%						
Isokineticity	%						
Particulate loading	mg/dscm gr/dscf						
Carbon monoxide	ppm						
Carbon dioxide	%						
Oxygen	%						
HCl	ppmv						
NO_x	ppmv						
SO_2	ppmv						

TABLE 4-5. EXAMPLE PRO FORMA TABLE FOR DICXINS AND FURANS EMISSION DATA

Compound or homolog	Method[a]	Units	Run 1	Run 2	Run 3	Mean	RPD	Comment/reference
Total TCDDs		ng/Nm³[b]						
2,3,7,8-TCDD		ng/Nm³						
Total PeCDDs		ng/Nm³						
2,3,7,8-PeCDDs		ng/Nm³						
Total HxCDDs		ng/Nm³						
2,3,7,8-HxCDDs		ng/Nm³						
Total HpCDDs		ng/Nm³						
2,3,7,8-HpCDDs		ng/Nm³						
OCDD		ng/Nm³						
Total TCDFs		ng/Nm³						
2,3,7,8-TCDF		ng/Nm³						
Total PeCDFs		ng/Nm³						
2,3,7,8-PeCDFs		ng/Nm³						
Total HxCDFs		ng/Nm³						
2,3,7,8-HxCDFs		ng/Nm³						
Total HpCDFs		ng/Nm³						
2,3,7,8-HpCDFs		ng/Nm³						
OCDF		ng/Nm³						
Total 2,3,7,8-TCDD equivalents[c]								

[a] Method reference, e.g., MM5/SW-846 or MM5/GC/MS.

[b] Dry normal at 7% O_2.

[c] Citation for equivalents calculation.

TABLE 4-6. EXAMPLE PRO FORMA TABLE FOR METALS EMISSION DATA

Element	Method[a]	Units	Run 1	Run 2	Run 3	Mean	RPD	Comment/reference
Lead		$\mu g/Nm^3$						
Mercury		$\mu g/Nm^3$						
Cadmium		$\mu g/Nm^3$						
Chromium		$\mu g/Nm^3$						
Others: (list)								

[a] EPA method number (e.g., M12) or description (e.g., M5/SW-846 3050/ICP).

[b] Dry normal at 7% O_2.

TABLE 4-7. PRO FORMA TABLE FOR OTHER ORGANICS EMISSION DATA

Compound or homolog	Method[a]	Units	Run 1	Run 2	Run 3	Mean	RPD	Comment/reference
		ng/Nm^3[b]						

[a] Method reference, e.g., MM5/SW-846 or MM5/GC/MS.

[b] Dry standard at 7% O_2.

TABLE 4-8. EXAMPLE PRO FORMA TABLE FOR DATA QUALITY RESULTS

Parameter	Criterion	Data quality objective	Data quality results	Comment/reference
2,3,7,8-TCDD	MM5 isokineticity	90-110%		
	MIS recovery	50-150%		
	Detection limit	0.15 ng/Nm^3		
	QC check sample accuracy	60-120%		
	MIS precision	< 50% RSD		
Lead	M5 isokineticity	90-110%		

SECTION 6.0

ADDITIONAL SOURCES OF INFORMATION

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APPENDIX A

ADDITIONAL MEASUREMENT METHODS FOR RESEARCH TESTING

1.0 POLYCHLORINATED BIPHENYLS

The methods presented in this section are appropriate for measuring polychlorinated biphenyls (PCBs) in MWC stack emissions. Monochloro through decachloro PCBs are determined by homolog.

1.1 METHOD DESCRIPTION

Stack emission samples are collected for PCB measurement using an MM5 train identical to that described in Section 3.1 of this document for measuring PCDDs and PCDFs. The sample components recovered from the train are extracted, the extracts are combined and cleaned to remove excessive levels of potential interferences, and the cleaned extracts are analyzed for PCBs by homolog using GC/MS.

1.1.1 Sample Collection

The MM5 train configuration, preparation, operation, and sample recovery described for determining PCDDs and PCDFs in MWC stack gases (Section 3.1 of this document) can be directly applied to measuring PCBs.

1.1.2 Sample Analysis

A primary reference for determining PCBs in MWC stack samples by homolog is EPA Method 680. The GC/MS analysis procedure was previously described by Erickson *et al.* Method 680 addresses PCB measurements in water and soil/sediment by GC/MS. Although the sample preparation, extraction, and extract cleanup requirements for MWC stack samples differs somewhat from water and soil/sediment samples, the GC/MS-SIM analysis and quantitation protocol presented in Method 680 are directly applicable.

1.1.2.1 Sample Preparation and Extraction--

Preparation and extraction of MM5 sample components described for PCDDs and PCDFs (Section 3.1.1.2 of this document) can be directly applied to samples for PCBs with two exceptions. Samples for PCB determination must be spiked with a solution of surrogate recovery standards rather than the PCDD and PCDF MIS solution. Also, MM5 resin and particulate samples can be extracted for PCBs using dichloromethane rather than toluene or benzene.

The PCB surrogate compounds are used only to assess PCB recoveries rather than as the method internal standards used for PCDDs and PCDFs. PCB quantitation does employ an internal standard spiked just prior to GC/MS analysis. The PCB surrogate solution should contain at least four ^{13}C-labeled congeners representing different homologs. The spike level should be in the range of 5 to 10 times the anticipated detection limit. Example labeled congeners which may be used as recovery surrogates include the following:

$^{13}C_6$-4-monochlorobiphenyl
$^{13}C_{12}$-3,3',5,5',6,6'-octachorobiphenyl
$^{13}C_{12}$-2,2',3,3',5,5',6,6'-octachlorobiphenyl
$^{13}C_{12}$-decachlorobiphenyl

Since the sample preparation and extraction of MM5 samples for PCBs is the same as for PCDDs and PCDFs, the combined extract from a single train (resin and particulates must be extracted with toluene or benzene) can be split to accommodate the two analyses. However, splitting the extract increases the potential detection limits for both sets of analytes.

Unequal splitting can be employed, depending on target detection limits.

1.1.2.2 Extract Cleanup--

The extracts from each MM5 train should be combined, dried by passage through a short column of anhydrous sodium sulfate, and concentrated to 5 mL using Kuderna-Danish evaporators. A 15-mL aliquot of hexane should be added and the extract concentrated to 2 mL using Kuderna-Danish evaporators and nitrogen blowdown. The concentrated extract should then be cleaned by chromatography prior to GC/MS analysis. A detailed protocol for cleanup using florisil is presented in Method 3620, SW-846. A silica gel cleanup procedure, as described in Method 3630, SW-846 can also be used. The cleaned extract should be concentrated to 500 µL using Kuderna-Danish evaporators and nitrogen blowdown.

1.1.2.3 GC/MS Analysis--

Sample extracts must be analyzed by GC/MS using a fused silica capillary column and selected ion monitoring (SIM) data acquisition. A detailed protocol is presented in Method 680. The recommended capillary column is a 30-m DB-5 or SE-54.

PCBs and recovery surrogate compounds are quantitated in the extracts using response factors normalized to internal standard compounds spike into the cleaned extract just prior to analysis. The relative response factors (RRFs) are determined by analyzing at least three levels of calibration solutions prior to sample analysis. The calibration solutions should contain the native PCB congeners, retention time calibration compounds, and internal standard compounds shown in Table A-1. The levels of the native congeners should cover a 100-fold concentration range and the lowest concentration should be 5 times the practicable detection limit. The retention time calibration and internal standard compounds should be present at the same level in all solutions. The calibration solutions should also contain the recovery surrogate compounds at concentrations corresponding to the spike level in samples.

The RRFs for the native congeners and recovery surrogates should agree with a relative standard deviation (RSD) of 20% for all compounds. Once acceptable calibration has been achieved, it is verified each day of analysis by analyzing the mid-level standard at the beginning and end of the day. RRFs for the daily standards must be within 20% of the calibration RRFs, otherwise recalibration is necessary.

The concentrations of mono through decachlorobiphenyl homologs are determined using their RRFs and are reported as mass of homolog per sample volume, e.g., nanogram of tetrachlorobiphenyl per normal cubic meter (ng/Nm^3). Detection limits should be determined for each homolog not detected using a response of 2.5 times the background noise signal at the appropriate retention time. The recoveries of the surrogate compounds are also quantitated using RRFs. The surrogate recoveries should be within the range of 50 to 150%. Recoveries outside this range may indicate problems in the analysis.

1.2 CRITICAL FEATURES

1.2.1 Sample Collection

The critical features of MM5 sample collection for PCBs are essentially the same as those for PCDDs and PCDFs, as described in Section 3.1.2.1 of this document.

1.2.2 Sample Analysis

The critical features of analysis of MWC stack samples for PCBs are somewhat

TABLE A-1. CALIBRATION COMPOUNDS CONTAINED IN PCB STANDARD SOLUTIONS

PCB homolog	Congener number[a]	Chlorine substitution
Concentration Calibration Standard		
Monochlorobiphenyl	1	2
Dichlorobiphenyl	5	2,3
Trichlorobiphenyl	29	2,4,5
Tetrachlorobiphenyl	50	2,2',4,6
Pentachlorobiphenyl	87	2,2',3,4,5'
Hexachlorobiphenyl	154	2,2',4,4,',5,6'
Heptachlorobiphenyl	188	2,2',3,4',5,6,6'
Octachlorobiphenyl	201	2,2',3,3',4,5',6,6'
Nonachlorobiphenyl	207	2,2',3,3',4,4',5,6,6'
Decachlorobiphenyl	209	2,2',3,3',4,4',5,5',6,6'
Retention Time Calibration Standards		
Tetrachlorobiphenyl	77	3,3',4,4'
Pentachlorobiphenyl	104	2,2',4,6,6'
Nonachlorobiphenyl	208	2,2',3,3',4,5,5',6,7'
Internal Standards		
d_{10}-anthracene		
d_{12}-chrysene		
d_6-3,3',4,4',-tetrachlorobiphenyl		

[a] Numbered according to system of Ballschmiter and Zell (Ballschmiter, K., and M. Zell, *Fresenius Z. Anal. Chem.*, 302, 20, 1980.

typical for analyses of trace contaminants in environmentally-related samples in general. The principal considerations are the potential for sample contamination and analyte losses. For example, significant losses of PCBs (or even PCDDs and PCDFs) can result from allowing an extract to evaporate to dryness.

1.3 QUALITY ASSURANCE ABN QUALITY CONTROL PROCEDURES

The primary quality assurance and quality control procedures that should be employed for PCB determinations in MWC stack samples are essentially the same as described for PCDDs and PCDFs in Section 3.1.3 of this document. Procedures for calibration of field equipment, field lab blank samples, laboratory blank samples, resin prescreening, and quality control check samples are identical. RRFs should be monitored in a similar manner.

1.4 DATA QUALITY OBJECTIVES

1.4.1 Limit of Detection

As in the case of PCDD and PCDF measurements (Section 3.1.4.1 of this document) objectives for limits of detection should be based on regulatory requirements. Table A-2 presents target limits of detection for PCB homologs that are readily achievable using the methods described above with a high performance quadrupole GC/MS system. Significantly lower detection limits have been achieved for some MWC tests.

1.4.2 Accuracy

The accuracy objective for blind quality control check samples is 60 to 120% of the spike level. The accuracy objective for recovery of surrogate compounds should be 50 to 150%.

1.4.3 Precision

Precision should be evaluated by pooling all the accuracy values, i.e., recoveries for each surrogate compound. For example, the recoveries for $^{13}C_{12}$-3,3',4,4'-tetrachlorobiphenyl should be pooled to determine a single precision value. The target for precision should be $\leq$ 50% RSD.

1.4.4 Completeness

The completeness objective for PCBs in MWC flue gases should be at least 90% valid determinations.

2.0 OTHER SEMIVOLATILE ORGANICS

These methods are appropriate for determining chlorinated benzenes (CBs), chlorinated phenols (CPs), and polycyclic aromatic hydrocarbons (PAHs) in MWC stack gases.

2.1 METHOD DESCRIPTION

Stack emissions are sampled for CB, CP, and/or PAH measurement using an MM5 train identical to that described in Section 3.1 of this document for determining PCDDs and PCDFs. The sample components are combined and cleaned to remove excessive levels of potential interferences (if required), and the extracts are analyzed using GC/MS.

2.1.1 Sample Collection

The MM5 train configuration, preparation, operation, and sample recovery described for determining PCDDs and PCDFs in MWC stack gases (Section 3.1 of this document) can be directly applied to measuring CBs, CPs, and/or PAHs.

TABLE A-2. EXAMPLE TARGET LIMITS OF DETECTION

Congener	Target detection limit (ng/Nm^3)
Monochlorobiphenyl	5
Dichlorobiphenyl	5
Trichlorobiphenyl	5
Tetrachlorobiphenyl	5
Pentachlorobiphenyl	10
Hexachlorobiphenyl	10
Heptachlorobiphenyl	10
Octachlorobiphenyl	15
Nonachlorobiphenyl	15
Decachlorobiphenyl	15

2.1.2 Sample Analysis

A primary reference for determining CBs, CPs, and/or PAHs in MWC stack samples is Method 8270, SW-846.

2.1.2.1 Sample Preparation and Extraction--

Preparation and extraction of MM5 sample components described for PCDDs and PCDFs (Section 3.1.1.2 of this document) can be applied nearly directly to samples for CBs, CPs, and PAHs. The only exceptions are the selection of extraction solvent, pH adjustment of aqueous samples prior to extraction, and surrogate recovery spiking. Extraction of the MM5 resin and particulate catch with toluene or benzene can cause significant losses of monochloro and dichlorobenzenes during subsequent extract concentration. Hence, extraction with dichloromethane is preferred if quantitation of these compounds is required. The aqueous samples must be adjusted to pH $\leq$ 2 with 50% aqueous sulfuric acid prior to extraction to ensure quantitative extraction of the more acidic CPs.

Prior to extraction, the sample components should be spiked with recovery surrogate compounds to facilitate assessment of analyte recoveries. GC/MS quantitation, as described in Method 8270, SW-846, employs internal standard compounds spiked just prior to GC/MS analysis. The surrogate solution should contain ^{13}C or deuterium-labeled representatives of each analyte class, as available. The spike level should be in the range of 5 to 10 times the anticipated detection limit. Several deuterium-labeled PAH compounds are available for use as recovery surrogates or internal standards for GC/MS quantitation. These include the following.

d_8-Naphthalene
d_{10}-Anthracene
d_{10}-Phenanthrene
d_{10}-Acenaphthene
d_{12}-Chrysene
d_{12}-Perylene

Example labeled compounds which may be used as recovery surrogates for CBs and CPs are shown below.

$^{13}C_6$-1,2,4,5-Tetrachlorobenzene
$^{13}C_6$-2,4,5-Trichlorophenol
$^{13}C_6$-Pentachlorophenol

Since the sample preparation and extraction of MM5 samples for CBs, CPs, and PAHs is the same as for PCBs, PCDDs, and PCDFs, the combined extract from a single train (resin and particulates must be extracted with toluene or benzene) can be split to accommodate multiple analyses. However, splitting the extract increases the potential detection limits for both sets of analytes. Also, using a single sample for all analytes compromises quantitation of monochloro and dichlorobenzenes since PCDD and PCDF determination requires extraction of the resin and particulate catch with toluene or benzene. Unequal splitting can be employed, depending on target detection limits.

2.1.2.2 Extract Cleanup--

Extract cleanup is typically required to achieve low detection limits for MWC stack samples. The extracts from each MM5 train should be combined, dried by passage through a short column of anhydrous sodium sulfate, and concentrated to 5 mL using Kuderna-Danish evaporators. A 15-mL aliquot of hexane should be added and the extract concentrated to 2 mL using Kuderna-Danish evaporators and nitrogen blowdown. If cleanup is not required, the extract should be further concentrated to 500 µL for GC/MS analysis.

A detailed protocol for cleanup of extracts for CBs using florisil is

presented in Method 3620, SW-846. A silica gel procedure for PAHs and derivatized CPs is described in Method 3630, SW-846. Either method can be used for CBs, CPs (underivatized), and PAHs. The cleaned extract should be concentrated to 500 µL using Kuderna-Danish evaporators and nitrogen blowdown.

2.1.2.3 GC/MS Analysis--

Sample extracts must be analyzed by GC/MS using a fused silica capillary column. A detailed protocol is presented in Method 8270, SW-846. The recommended capillary column is a 30-m DB-5. Method 8270, SW-846 specifies full scan data acquisition. Although full scan data facilitates compound identification confirmation by review of complete mass spectra, the levels of detection achievable are frequently insufficient for MWC stack samples. Hence, SIM data acquisition is recommended. The same characteristic ions and procedures described in Method 8270, SW-846 can be used directly, but data should be acquired in the SIM mode.

CBs, CPs, and PAHs and the recovery surrogate compounds are quantitated in the extracts using response factors normalized to internal standard compounds spike into the cleaned extract just prior to analysis. The relative response factors (RRFs) are determined by analyzing at least three levels of calibration solutions prior to sample analysis. The calibration solutions should contain the native analytes, recovery surrogates, and internal standard compounds. The internal standards should include 1-3 deuterium-labeled PAH compounds other than those used as recovery surrogates. The levels of the native analytes should cover a 100-fold concentration range and the lowest concentration should be 5 times the practicable detection limit. The calibration solutions should also contain the recovery surrogate compounds at concentrations corresponding to the spike level in samples.

The RRFs for the native analytes and recovery surrogates should agree with a relative standard deviation (RSD) of 20% for all compounds. Once acceptable calibration has been achieved, it is verified each day of analysis by analyzing the mid-level standard at the beginning and end of the day. RRFs for the daily standards must be within 20% of the calibration RRFs, otherwise recalibration is necessary.

The concentrations for each compound are determined using their RRFs and are reported for each individual compound as mass per sample volume, e.g., nanogram of 1,2,4,5-tetrachlorobenzene/dscm. Detection limits should be determined for each compound using a response of 2.5 times the background noise signal at the appropriate retention time. The recoveries of the surrogate compounds are also quantitated using RRFs. The surrogate recoveries should be within the range of 50 to 150%. Recoveries outside this range may indicate problems in the analysis.

2.2 CRITICAL FEATURES

2.2.1 Sample Collection

The critical features of MM5 sample collection for CBs, CPs, and PAHs are essentially the same as those for PCDDs, and PCDFs, as described in Section 3.1.2.1 of this document.

2.2.2 Sample Analysis

The critical features of analysis of MWC stack samples for CBs, CPs, and PAHs are somewhat typical for analyses of trace contaminants in environmentally-related samples in general. The principal considerations are the potential for sample contamination and

analyte losses. For example, significant losses can result from allowing an extract to evaporate to dryness. Also, PAH compounds are susceptible to photodegradation and should be protected from exposure to light.

2.3 QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

The primary quality assurance and quality control procedures that should be employed for CB, CP, and PAH determinations in MWC stack samples are essentially the same as described for PCDDs and PCDFs in Section 3.1.3 of this document. Procedures for calibration of field equipment, field lab blank samples, laboratory blank samples, resin prescreening, and quality control check samples are identical. RRFs should be monitored in a similar manner.

2.4 DATA QUALITY OBJECTIVES

2.4.1 Limit of Detection

As in the case of PCDD and PCDF measurements (Section 3.1.4.1 of this document) objectives for limits of detection should be based on regulatory requirements. Table A-3 presents target limits of detection for specific compounds that are readily achievable using the methods described above with a high performance quadrupole GC/MS system. Significantly lower detection limits have been achieved for some MWC tests.

2.4.2 Accuracy

The accuracy objective for blind quality control check samples is 60 to 120% of the spike level. The accuracy objective for recovery of surrogate compounds should be 50 to 150%.

2.4.3 Precision

Precision should be evaluated by pooling all the accuracy values, i.e., recoveries for each surrogate compound. For example, the recoveries for $^{13}C_6$-2,4,5-trichlorophenol should be pooled to determine a single precision value. The target for precision should be $\leq$ 50% RSD.

2.4.4 Completeness

The completeness objective for PCBs in MWC flue gases should be at least 90% valid determinations.

3.0 VOLATILE ORGANICS

These methods are generally appropriate for measuring organics with boiling points in the range of 30°to 100°C in MWC stack emissions. Compounds with boiling points as as high as 145°C may also be determined. Some compounds with boiling points lower than 30°C can also be determined, although significant breakthrough may occur causing underestimation of concentrations.

3.1 METHOD DESCRIPTION

The method involves passing the stack gases through adsorbent cartridges. The volatile organics retained by the cartridges are transferred to the laboratory where the analytes are thermally desorbed from the cartridges and determined by GC/MS.

3.1.1 Sample Collection

Samples are collected using the volatile organics sampling train (VOST). A detailed protocol for VOST sampling can be found in Method 0030 of SW-846.

TABLE A-3. EXAMPLE TARGET LIMITS OF DETECTION

Compound	Target detection limit (ng/Nm^3)
Chlorobenzenes	
1,3-Dichlorobenzene	10
1,4-Dichlorobenzene	10
1,2-Dichlorobenzene	10
1,3,5-Trichlorobenzene	10
1,2,4-Trichlorobenzene	10
1,2,3-Trichlorobenzene	10
1,2,3,4-Tetrachlorobenzene	10
1,2,3,5-Tetrachlorobenzene and 1,2,4,5-Tetrachlorobenzene	10
Pentachlorobenzene	10
Hexachlorobenzene	10
Chlorophenols	
2-Chlorophenol	10
3-Chlorophenol and 4-Chlorophenol	10
2,3-Dichlorophenol	10
2,6-Dichlorophenol	10
3,5-Dichlorophenol	10
3,4-Dichlorophenol	10
2,4-Dichlorophenol and 2,5-Dichlorophenol	10
2,3,5-Trichlorophenol	10
2,4,6-Trichlorophenol	10
2,4,5-Trichlorophenol	10
2,3,4-Trichlorophenol	10
2,3,6-Trichlorophenol	10
2,3,5,6-Tetrachlorophenol	15
2,3,4,5-Tetrachlorophenol	15
Pentachlorophenol	50
Polycyclic Aromatic Hydrocarbons	
Nathphalene	20
Acenaphthylene	5
Acenaphthene	15
Fluorene	15
Phenanthrene	20
Anthracene	20
Fluoranthene	20
Pyrene	20
Benz[a]anthracene	20
Chrysene	20
Benzo[b]fluoranthene	30
Benzo[k]fluoranthene	30
Benzo[a]pyrene	30
Indeno[1,2,3-cd]pyrene	30
Dibenz[a,h]anthracene	30
Benzo[g,h,i]perylene	30

3.1.1.1 Train Configuration--

The primary components of the VOST system are the probe, condenser, condensate trap, a second condenser, and a backup resin trap. A schematic of the VOST system is shown in Figure A-1. Figure A-2 shows a drawing of the train. The first cartridge is packed with approximately 1.6 g of Tenax-GC resin. The second cartridge is packed with Tenax-GC and petroleum-based charcoal (1 g of each, approximately 3:1 by volume) with the charcoal on the outlet end. The first trap retains most of the higher boiling analytes. Lower boiling analytes and the portion of the higher boiling analytes that break through the first cartridge are retained on the second trap. Analytes that collect in the condensate trap are purged into the second condenser and trap units.

Design details of the traps may differ as appropriate for the specific fittings used for the train and for the specific design of the thermal desorption unit used to analyze the contents of the traps. An example trap design is shown in Figure A-3.

3.1.1.2 Adsorbent Cartridge Conditioning

Prior to use, both new and previously used adsorbent cartridges must be conditioned and checked for background contamination. This involves heating the traps to 190°C and passing organic-free nitrogen through the traps (in the reverse of the sampling direction) at ≥ 40 mL/min for 12-28 h. The conditioned traps are then analyzed for background contamination by thermal desorption and GC/FID detection. This procedure is described in Method 0030, SW-846. A convenient alternative is to continuously measure the trap background by analyzing the gas exiting the traps during conditioning. The exit gases from a trap can be sampled using a gas sampling valve and introduced onto a "dummy" column (3-m x 1/16-in OD SS tubing). The FID response should be equivalent to < 5 ppb propane.

3.1.1.3 Train Operation--

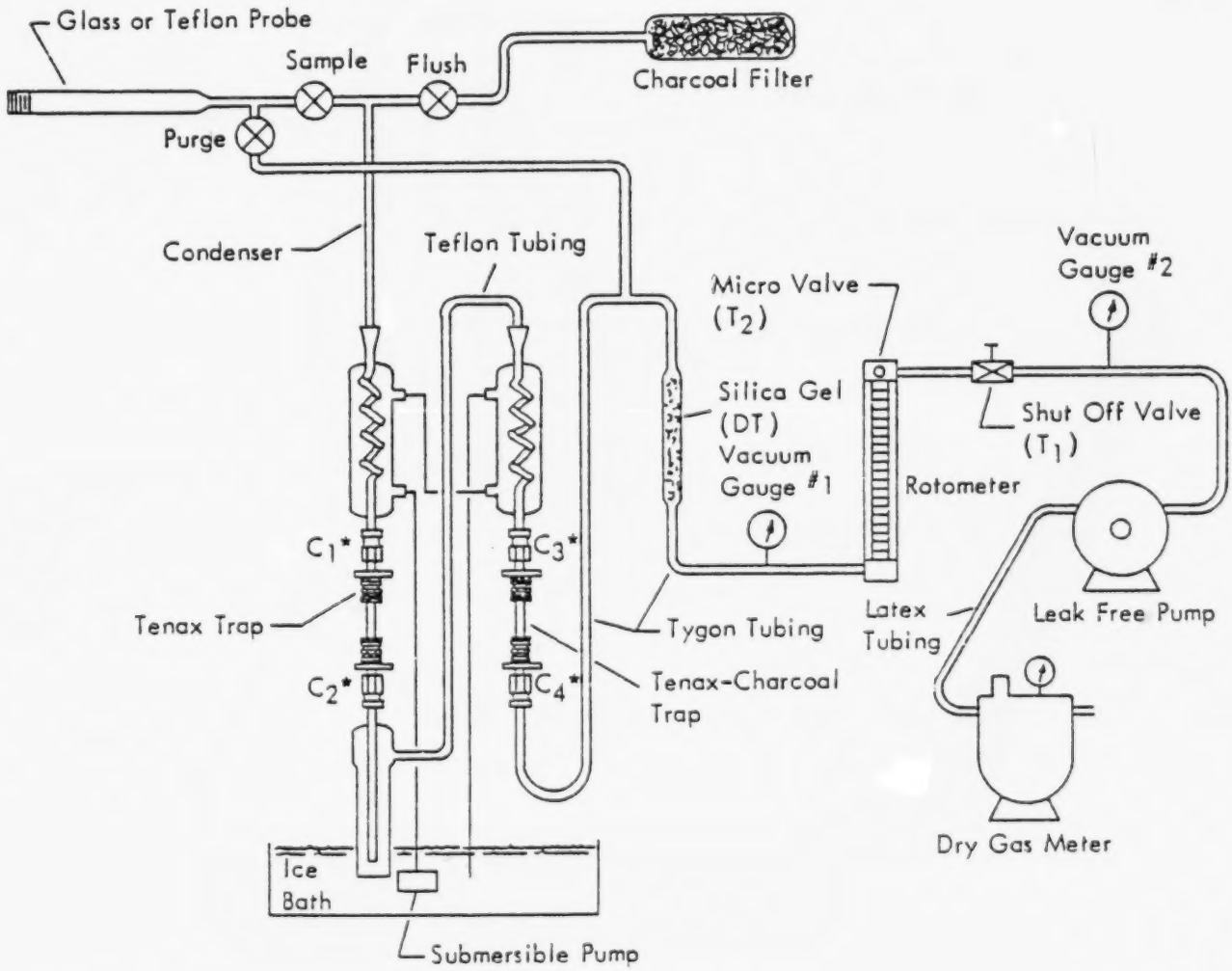
The sampling flow rate should be approximately 1 L/min for 20 min for a total of 20 L. The traps should be removed, a new pair installed, and sampling continued at the same rate. A total of six pairs of traps should be used. Alternatively, the sampling rate can be reduced to as low as 0.25 L/min to extend the sampling period. The total sampling time should not be less than 1 h and at least 3 pairs of traps should be used. The total volume sampled by a pair of traps should not exceed 20 L. All traps should be tightly sealed and stored at ice temperature until analysis.

3.1.2 Sample Analysis

A detailed protocol for analysis of VOST traps can be found in Method 5040, SW-846. The volatile organic contents of the traps are thermally desorbed and analyzed by GC/MS. Method 8240, SW-846, describes the GC/MS system and procedures.

The design of the thermal desorption units may differ for various adsorbent trap designs. However, the desorption unit must be leak-free and direct the gas flow through the cartridge in the reverse of the sample collection flow.

Prior to desorption and analysis, each trap is spiked with an internal standard solution (in methanol). The internal standard compounds should be stable isotope-labeled analogs of the compounds of interest or similar compounds. Typical internal standards include d_6-benzene, d_{10}-ethylbenzene, and d_4-dichloroethane.



* Viton O-Ringed Nickel Plated Fittings

Figure A-1. Schematic of the volatile organic sampling train (VOST) (from Method 0030, SW-846).

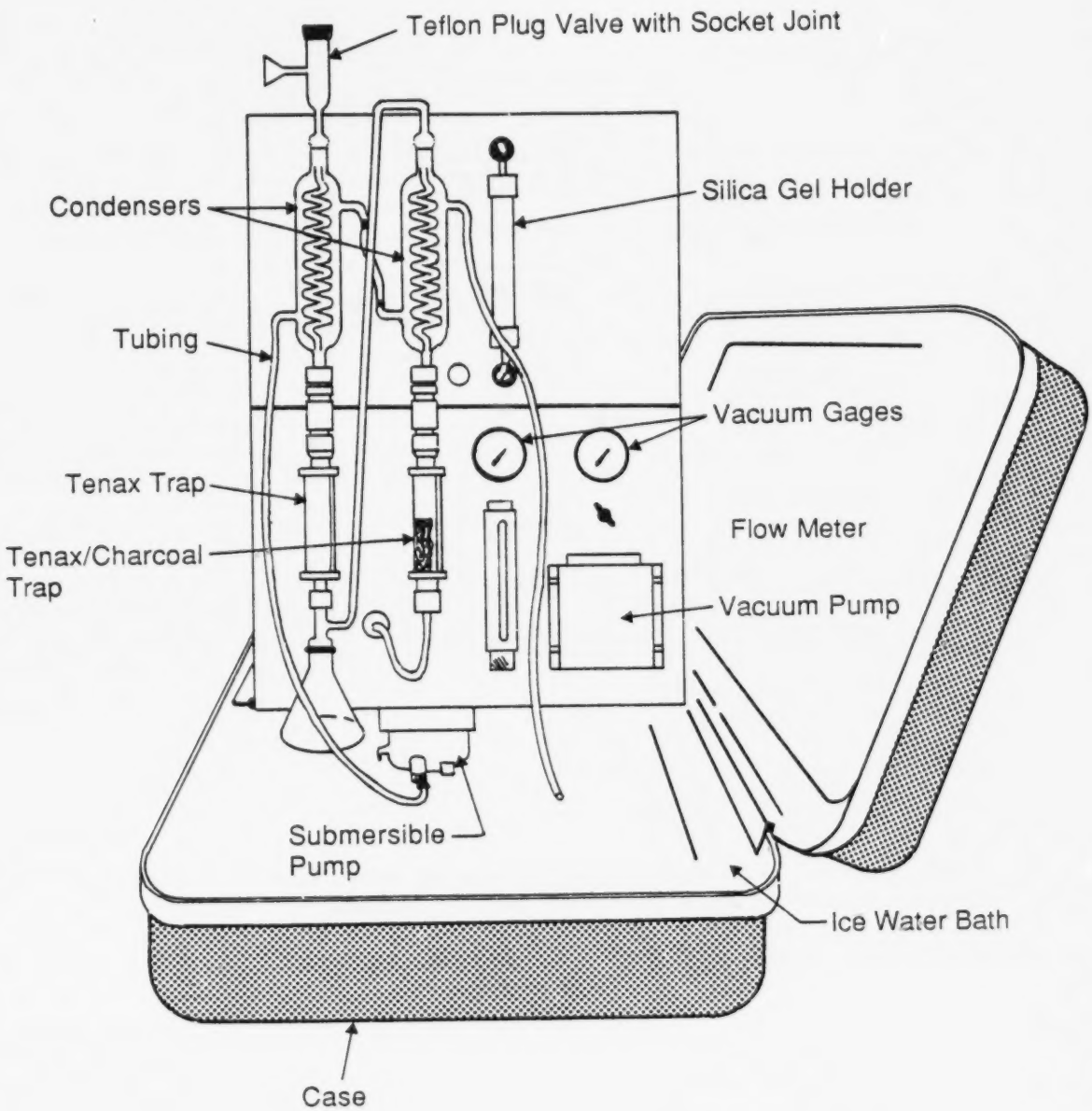


Figure A-2. VOST system setup (from Method 0030, SW-846).

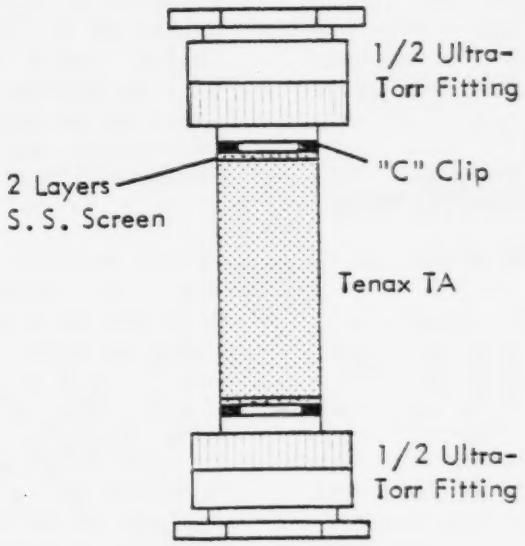


Figure A-3. VOST trap assembly (EPA 600/9-84-019, November 1984, Proceedings: National Symposium on Recent Advances in Pollutant Monitoring of Ambient Air and Stationary Sources, pp. 171-179, "Volatile Organic Sampling Train (VOST) Development at MRI by Fred Bergman).

Following desorption of the sample from the VOST trap onto the analytical trap, the contents of the analytical trap are thermally desorbed onto the GC/MS system. The GC/MS data are acquired using the scanning mode. SIM data acquisition can be used to decrease limits of detection. Analytes are quantitated using relative response factors (relative to the internal standards) determined by analyzing standard solutions of the analytes (in methanol) spiked onto a blank VOST trap. Detection limits should be determined for each compound not detected using a response of 2.5 times the background noise signal at the appropriate retention time.

The relative response factors (RRFs) should be determined from at least three levels of standard solutions over a 100-fold range. The lowest standard level should be approximately 5 times the detection limit. The RRFs should agree within a relative standard deviation of 20%. Once an acceptable calibration is achieved, it is verified each day of sample analysis by analyzing the mid-level standard at the beginning and end of the day. RRFs for the daily standards must be within 20% of the calibration RRFs; otherwise, recalibration is necessary. Alternatively, control charts can be used to monitor RRFs.

VOST trap samples and field blanks should be analyzed within 14 d of sampling. Analysis results from traps held longer than 14 d may be considered suspect for some compounds.

3.2 CRITICAL FEATURES

Avoiding contamination of samples and standards is crucial to successful VOST sampling and volatiles analysis. Adsorbent cartridges and analytical standards should be prepared in a clean laboratory that is practically solvent-free. Adequate cleaning of the traps prior to use and avoiding contamination during field handling, shipment to the analysis laboratory, and storage prior to analysis are especially critical. Each trap should be screened to ensure that the background is acceptable immediately following precleaning. Clean traps should be stored in sealed metal cans with an activated charcoal packet in the can. Immediately following sampling, the used traps should also be stored in sealed cans with activated charcoal. However, clean and used traps must not be stored in the same can.

3.3 QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

3.3.1 Field Blank Samples

At least one pair of blank traps should be analyzed for each test run. The blank traps should be taken to the sampling site and opened, i.e., end caps removed, for a time period typically required for changing traps in the VOST train. The caps should be replaced and the blank traps shipped to the analysis laboratory for analysis. Also, a pair of trip blank traps should be analyzed for each MWC facility test. Trip blanks are handled similar to other field blank samples, although the end caps are not removed.

3.3.2 Laboratory Blank Samples

A laboratory blank sample, i.e., blank trap, must be analyzed at the beginning of each day standards or samples are analyzed to check the background attributable to the VOST trap desorption and purge-trap-GC/MS systems. The laboratory blank should be spiked with the internal standard solution.

3.3.3 Relative Response Factor Monitoring

Relative response factors must be monitored for each analyte. The RRFs for the daily standards should fall within 20% of the mean from the calibration RRFs. Alternatively, RRF control charts can be maintained. A mid-level standard should also be analyzed in triplicate to determine precision. The relative response factors should agree within ±20%.

3.3.4 Quality Control Check Standards

A blind quality control check standard should be analyzed with samples from each facility test. The check standard should be spiked onto a VOST trap. The analyte concentrations should be within the lower half of the calibration range. The accuracy results for blind check standards should be within 60-120% of the spiked level.

If available, audit gas samples may also be analyzed. Audit gas samples are provided by the EPA's Environmental Monitoring Support Laboratory, Research Triangle Park, North Carolina (at the request of the permitting authority) for VOST performance audits related to hazardous waste incinerator trial burns. The audit gas cylinder is sampled using a VOST train and the traps are analyzed as samples.

3.4 DATA QUALITY OBJECTIVES

3.4.1 Limits of Detection

Limits of detection for volatiles differ somewhat by compound. Target detection limits for most volatile organics using scan mode GC/MS should be in the range of 0.1-5 $\mu g/Nm^3$. Significantly lower detection limits have been achieved for some MWC tests.

3.4.2 Accuracy

The accuracy objective for blind control check samples is 60-120% of the spike level.

3.4.3 Precision

Precision is determined from triplicate analysis of a standard solution. The RRFs should be within ±20% for all analytes.

3.4.4 Completeness

The completeness objective for volatile organics in the MWC flue gases should be at least 90% valid determinations.

4.0 METALS

4.1 ARSENIC AND NICKEL

4.1.1 Method Description

It is the consensus of the Work Group that samples be collected for arsenic and nickel using EPA Method 12, described in Section 3.3.1 of the body of this document under Lead, Cadmium, and Total Chromium. After sample collection, recovery, and digestion as specified in Method 12, arsenic is determined by hydride generation AAS and nickel by ICP or AAS.

4.1.2 Critical Features

The critical features discussed under M12 for lead, cadmium, and total chromium matter determinations apply to arsenic and nickel concentration measurement as well. It is expected that most arsenic and nickel in MWC emissions will be associated with the particulate matter.

Each lot of glass fiber filters used in the sampling train should be checked prior to field testing to confirm that background levels are low. Polytetrafluoroethylene (PTFE) coated glass fiber filters may be used.

When sampling at source locations containing high HCl levels (especially at facilities without acid gas removal or at points upstream of the acid gas removal system), use of a stainless steel buttonhook nozzle may lead to unacceptably high nickel contamination. Use of quartz nozzle is recommended for all nickel determinations.

The detection limit for arsenic by cold vapor AAS is on the order of 1-2 µg/L in the solution as analyzed. Assuming a standard sample of 1.1 m^3, and a final digested sample volume of 250 mL each for the probe, filter, and impinger contents of the train (as in Method 108), this corresponds to an in-stack detection limit of 0.15 to 0.3 µg/m^3. If lower detection limits are required to meet the test objectives, the most promising alternative is to collect a larger stack gas sample. For arsenic, neither furnace AAS nor ICP offer a substantially lower detection limit than that obtainable by hydride generation.

The detection limit for nickel determination by flame AAS is about 40 µg/L. Assuming a standard M5 stack gas sample volume of 1.1 m^3 and a final digested sample volume of 250 mL (as specified in M12), this corresponds to an in-stack detection limit of 9 µg/m^3. If lower detection limits are required to meet the test objectives, options include:

- Collection of a larger stack gas sample,
- Use of a smaller volume for the digested sample dilution, or
- Substitution of ICP for the AAS analysis.

The sensitivity enhancement possible by using these options are, respectively, a factor of 2-3, a factor of 2-5, and a factor of 3.

4.1.3 Quality Assurance and Quality Control Procedures

4.1.3.1 Calibration--

The sampling equipment must be calibrated as specified in M5. Laboratory balances must be calibrated according to a regular schedule. The AAS system is calibrated for wavelength accuracy according to the manufacturer's specifications.

Quantification should be accomplished by reference to an external standard curve based on at least five standards covering the range from 0 to 25 µg As/L. Samples must be diluted as necessary to fall within the calibration curve range. The calibration curve should not be force-fit through zero.

4.1.3.2 Blanks--

A filter blank should be created using two filters from each lot used in the sampling train. The filter blank is digested in the same way as the samples. If the impinger solutions are included in the analysis, the blank should include a volume of 0.1 N nitric acid equal to that charged to the impingers. Blanks of the impinger water and the solution(s) used for rinsing the sampling train should be analyzed.

Replicates. Samples, standards, and blanks should be analyzed at least in duplicate. It is common practice to base compliance determinations on the mean of the arsenic and/or nickel emissions as measured in three separate stack sampling runs.

4.1.3.3 Spikes--

As with other metal determinations, it is not standard practice to analyze true "spikes", in which a known quantity of the metal is added to an aliquot of the sample prior to digestion. However, it is considered good practice to analyze at least one sample from each source by the method of standard additions.

4.1.3.4 Audit Samples--

It is recommended that quality control procedures include the analysis of at least two unknown arsenic audit samples from the EPA Quality Assurance Office. These should be analyzed concurrently with the field samples. As a preliminary check on laboratory performance, audit samples of known concentration are available through the EPA Environmental Systems Laboratory at Research Triangle Park.

4.1.3.5 Calculations--

The concentration of arsenic and/or nickel in the stack gas, Cs, is calculated as follows:

$$Cs\ (\mu/m^3) = \frac{Ca\ (\mu/L) \times D \times V_a\ (L)}{V_s\ (m^3)},$$

where

C_a = concentration in the solution as analyzed, from the calibration curve,
D = dilution factor(s), if any,
V_a = volume of digested sample, and
V_s = volume of stack gas sample.

4.1.4 Data Quality Objectives

No numerical data quality objectives have been established for the determination of arsenic or nickel in MWC emissions.

It is expected that the precision of replicate analyses of the same digested sample should not exceed 5% CV. The accuracy of the determination, as estimated by the method of standard additions, should be similar to that described for lead (Section 3.3 of this document).

4.2 BERYLLIUM

4.2.1 Method Description

The basic method for beryllium determination is EPA Method 104. This uses the same sampling train configuration as M5. However, the method specifies the use of a cellulose acetate membrane filter (e.g., Millipore AA), backed-up be a glass fiber filter if necessary to prevent tearing, for collection of beryllium. The sample is collected isokinetically. A minimum sampling time of 2 h is recommended.

Following sample collection and recovery, the filter is digested with concentrated nitric acid, followed by a sulfuric acid/perchloric acid digestion. The probe wash is combined with the contents of the first three impingers (water), evaporated to dryness, and digested in the same way as the filters. After digestion, the residues are combined and diluted with 25% HCl. The solution is analyzed by flame AAS.

4.2.2 Critical Features

The cellulose acetate membrane filter specified in M104 may not withstand the temperature and corrosion conditions in MWC effluent. A glass fiber filter may be used provided that the analysis of a representative number of filters from each lot shows acceptable background levels of Be. Note that the digestion procedure specified for Be ($HNO_3/H_2SO_4/HClO_4$) is not the same as that in the other metals methods (HNO_3/H_2O_2). It is acceptable to take a portion of the total sample from,

e.g., the lead digestion, and subject it to a subsequent Be digestion according to M104.

The critical features discussed under M5 (Section 3.2.2 of this document) for particulate apply to beryllium sampling as well.

The detection limit for Be using flame AAS is on the order of 5 µg/L in the solution as analyzed. Assuming the recommended 2-h sampling time (M5 sample volume of 2.2 m^3 and a digested sample volume of 10 mL, as specified in M104, this corresponds to an in-stack detection limit of 0.025 µg/m^3. However, these limits apply to clean (water) samples. The Be analysis is subject to interference from aluminum, magnesium, and silicon, all of which may be present in MWC stack particulate matter. The actual detection limits observed for MWC stack gas samples may therefore be considerably higher than 0.025 µg/m^3.

If even lower detection limits were required to meet the test objectives, either furnace AAS or ICP could be substituted as the analytical finish. The detection limits cited in SW-846 are 0.2 µg/L for furnace AAS and 0.5 µg/L for ICP.

4.2.3 Quality Assurance and Quality Control Procedures

Method 104 specifies the use of a single calibration standard of 1 µg/L Be concentration. However, for measurement of Be in MWC effluents, the use of a minimum 5-point calibration curve is advised.

Method 104 provides no guidance on analysis of blanks, replicates, or spikes. For MWC effluent characterization, it is recommended that blanks, spikes (analysis be method of standard additions), and replicates be included in the QAPP. The procedures specified for other metals (e.g, lead, chromium) can be used as guidelines for frequency and types of QC samples.

M104 specifies that the mean of three tests runs be used for the determination of compliance. For purposes of MWC combustion research and development testing, the same approach is recommended.

M104 presents the equation for calculating the Be emission rate on g/day. For MWC sampling, the equation shown above for arsenic determination should be substituted.

4.2.4 Data Quality Objectives

There are no numerical data quality objectives specified in M104 for accuracy or precision of Be determinations. The precision achievable should be comparable to that for other metals. However, for quantities near the detection limit, precision may be poorer due to nonspecific absorption and light scattering effects at the analytical wavelength.

4.3 CHROMIUM (VI)

4.3.1 Method Description

The NESCAUM consensus method for determination of hexavalent chromium in MWC effluents is the draft method developed by EPA's Environmental Monitoring Support Laboratory at Research Triangle Park, North Carolina. In this method, particulate chromium is collected in the probe and filter of a standard M5 train, sampling isokinetically. Glass fiber filters or PTFE-coated glass fiber filters may be used. After sample collection and recovery according to standard M5 procedures, the probe rinse and filter samples are combined, evaporated to dryness, and digested with a solution of 2% NaOH and 3% Na_2CO_3 in deionized distilled water.

The digested solution is brought to volume and the Cr(VI) determined colorimetrically as its diphenylcarbizone derivative. This analytical procedure is described in SW-846 Method 7196.

4.3.2 Critical Features

All of the critical features discussed under M5 (Section 3.2.2 of this document) sampling apply to the Cr(VI) determination.

For determination of chromium(VI), it is especially critical that replicate filters from each lot of filter medium be analyzed prior to testing to confirm that background levels of Cr(VI) are acceptably low.

In sampling MWC effluents containing high levels of HCl, especially when there is no acid gas removal or the sampling point is upstream of the acid gas removal system, stainless steel probe nozzles should not be used. Quartz is a recommended substitute.

The detection limit of the method is stated to be 50 µg/100 mL, with 100 mL as the standard volume for the digested sample. For a standard M5 sample of 1.1 m^3, this corresponds to an in-stack detection limit of 45 µg/m^3. However, some NESCAUM Work Group members have observed that interferences have caused precipitate formation and/or cloudiness of the solution. These difficulties may increase the practical limit of quantitation.

4.3.3 Quality Assurance and Quality Control Procedures

4.3.3.1 Calibration--

The sampling equipment is to be calibrated as described in M5. Laboratory balances should be calibrated according to a regular schedule. The spectrophotometer used for the colorimetric analysis is calibrated according to the manufacturer's recommendations. The EPA draft method specifies that a five-point calibration curve covering the range from 0 to 2,500 µg/L. This should be adequate for MWC emission measurement.

4.3.3.2 Blanks--

The draft method does not specify procedures for blanks other than a zero, i.e., 0.0 µg/L, calibration standard. For MWC testing, it is recommended that a blank consisting of 2 filters from each lot used in the sampling train be analyzed along with the samples.

4.3.3.3 Replicates--

The opportunity for replicate analysis is limited because the method specifies that 50 mL from the 100 mL total digested sample volume be used for each analysis. For characterizing the Cr(VI) concentration in MWC emissions, the mean of three replicate sampling and analysis runs should be used.

4.3.3.4 Spikes--

As for other EPA metals analysis procedures, the method specifies that at least one sample from each source be analyzed by the method of standard additions. The procedure is the same as that specified in M12 for lead.

4.3.4 Data Quality Objectives

Data quality objectives for isokineticity, leak check, etc., are as specified in M5.

No numerical data quality objective for precision has been established. However, EPA tests at a ferrochrome smelter, a chemical plant, and a refractory brick plant gave relative standard deviations of 4.4, 8.3, and 13.3%.

The numerical data quality objective for accuracy is stated in terms of the method of standard additions. The value of the Cr(VI) concentration calculated by that method must be within 5% of the value obtained by routine spectrophotometric analysis. If not, all samples must be analyzed by the method of standard additions.

4.4 MULTIPLE METALS SCREEN

4.4.1 Method Description

It is obvious that the sampling and sample preparation methods are the same or similar for many of the metals of potential interest with regard to MWC research and development. Recognizing this, the Environmental Monitoring Systems Laboratory at Research Triangle Park, North Carolina, has been developing a train for multiple metals sampling. The recommended configuration is an M5 train equipped with a nozzle, glass fiber filter, and five impingers as follows: (1) empty, (2 and 3) 5% HNO_3 and 10% H_2O_2 (will be reduced to 0.1 N HNO_3 if research shows it to be adequate), (4) 1.5% $KMnO_4$ and 10% H_2SO_4, and (5) silica gel. After sample collection and recovery, a nitric acid/hydrogen peroxide digestion as in M12 or SW-846 Method 3050 will convert most metals to solubie form. (Exceptions are: mercury, which would be lost through volatilization and is determined by the cold vapor AAS technique; beryllium, which requires a nitric/sulfuric/perchloric acid method for digestion; and chromium (VI), which requires a basic extraction method.)

For MWC research and development, the extract obtained from the nitric acid/hydrogen peroxide digestion can be screened by ICP to accomplish the determination of 25 different metals. These are:

Aluminum	Manganese
Antimony	Molybdenum
Arsenic	Nickel
Barium	Potassium
Beryllium	Selenium
Boron	Silicon
Cadmium	Silver
Calcium	Sodium
Chromium	Thallium
Cobalt	Vanadium
Copper	Zinc
Iron	
Lead	

The analytical procedure is presented in SW-846 Method 6010.

4.4.2 Critical Features

The features of the M5 train discussed in Section 3.2 of this document apply to the sampling of metals for ICP screening. Note that if silicon is to be determined, it is important that no silicone grease be used in sealing the train.

If chromium. iron and/or nickel are to be determined, the use of stainless steel nozzles is not recommended. Quartz should be substituted.

The detection limits for ICP analysis as given in Method SW-846 6010 range from 0.3 µg/L (Be) to 75 µg/L (Si). Assuming a standard M5 sample volume of 1.1 m^3 and a final digested sample volume of 250 mL, these correspond to in-stack detection limits of 0.07 µg/m^3 (Be) to 17 µg/m^3 (Si). For MWC that incorporate lime scrubbing for acid gas removal, levels of calcium in the stack particulate matter may be high. This could cause interference in the determination of other metals. It could also require serial dilution of the digested sample prior to calcium determination in order to get the concentration of calcium within the linear range of the ICP.

Note that while SW-846 lists arsenic and beryllium as elements to which the ICP screen applies, alternatives to the screening method described in this section are preferred for these elements. For arsenic, the AAS method is preferred because of the lower detection limit. For beryllium, an alternative digestion procedure is recommended.

4.4.3 Quality Assurance and Quality Control Procedures

It is recommended that calibration, blanks, replicates, spikes, and calculations for the ICP screen follow the guidelines given in Section 3.3 of this document for lead.

4.4.4 Data Quality Objectives

There are no established numerical data quality objectives for ICP screening of MWC emissions. These should be specified in the QAPP for each research and development program.

5.0 OTHER INORGANICS

5.1 FLUORIDE

5.1.1 Method Description

The Work Group recommends EPA Method 13B as the procedure for measurement of fluoride in MWC emissions. The sampling train in this method is essentially the same as in Method 5, except that the filter may be inserted at a different location with respect to the impingers and that a glass fiber filter is not used. Total fluoride collected in the train is determined by analysis using specific ion electrode. (Ion chromatography is an alternative method of determination.)

5.1.2 Critical Features

This method determines total fluoride, not just HF. Therefore, if permit limitations are expressed as HF concentrations, the appropriate regulatory authorities should be consulted to determine whether a modified or alternative procedure should be used.

The critical features discussed under M5 for particulate matter determinations apply to fluoride concentration measurement as well. For fluoride determinations, distilled deionized water is specified as the probe rinse solution for sample recovery. Prior to sample recovery, it is important that all M5 train surfaces potentially in contact with the sample be wiped free of grease, as residual grease could result in loss of fluoride.

The filter material selected should be paper or an organic membrane. Glass fiber filters will irreversibly react with HF and give erroneously low recoveries. For this reason, the Work Group does not recommend that fluoride determinations be performed on samples collected in the HCl train described earlier in this report. Three filters from each lot used for sampling should be analyzed prior to the test to confirm that the fluoride blank level is acceptably low.

The method notes that samples and standards should be at the same temperature (±2°C) to ensure accurate determinations.

The detection limit for fluoride cited in the method is 0.02 µ/mL (0.02 mg/L). However, concentrations lower than 0.1 (µg/mL require "extra care." Assuming then that 0.1 µg/mL represents a practical lower level of quantification, a 250 mL final sample volume and a 1:1 dilution with buffer as specified in Method 13B, the in-stack detection limit for a standard

1.1 m^3 M5 stack gas sample is about 11 µg/Nm^3 (0.011 mg/Nm^3).

5.1.3 Quality Assurance and Quality Control Procedures

5.1.3.1 Calibration--

The sampling equipment must be calibrated as specified in Method 5. Laboratory balances and pH meters must be calibrated according to a regular schedule.

The specific ion electrode calibration curve is prepared by analysis of 10^{-2}, 10^{-3}, 10^{-4}, and 10^{-5} **M** standard solutions of sodium fluoride and plotting electrode response (mv) against the logarithm of fluoride concentration. If the curve is nonlinear in the 10^{-4} to 10^{-5} **M** range, additional calibration standards at intermediate concentrations are added to the calibration curve.

5.1.3.2 Blanks--

As noted above under critical features, at least three filters from each lot should be analyzed as blanks; the acceptance level is specified as 15 µg (0.015 mg) F/cm^2 of filter area (Method 13A).

5.1.3.3 Replicates--

The method provides no specific guidance concerning field or laboratory replicate requirements. It is recommended that three sampling runs be performed and the average calculated for comparison with permit limitations, unless the regulatory authority specifies otherwise. The sample preparation procedure in the method provides a sufficient volume of final solution to allow replicate analytical measurements on each sample if required by the regulatory authority.

5.1.3.4 Spikes--

The method does not require the analysis of spikes. However, it is recommended that at least one sample from each source be analyzed by the method of standard addition.

5.1.3.5 Audit Samples--

If available, audit samples should be analyzed and the results reported along with sample data.

5.1.3.6 Calculations--

The equations for calculating the total fluoride content (mg/Nm^3) in the sample are provided in Methods 13A and 13B.

5.1.4 Data Quality Objectives

Method 13B provides guidance that a standard deviation of ±0.056 mg F/Nm^3 can be expected at fluoride concentrations of 0.1 to 1.4 mg/Nm^3 with five degrees of freedom (i.e., six samples). The collaborative study cited in the method did not find any bias in the analytical method. Therefore, the results of a method of standard additions check would be expected to give concentrations within 5 to 10% of those determined by direct measurement.

5.2 SULFUR TRIOXIDE/SULFURIC ACID MIST

5.2.1 Method Description

The Work Group did not reach a consensus on a method for measurement of sulfur trioxide/sulfuric acid mist in MWC emissions. The Work Group concluded that there has been insufficient method validation on this source category to allow a method to be recommended with confidence. Methods that were discussed as potentially applicable include EPA Method 8 (Method 5 approach with isopropanol in the first impinger, followed by a filter,

followed by hydrogen peroxide impingers), EPA Method 6 (a midget bubbler version of Method 8), controlled condensation, and a buffered formaldehyde impinger procedure provided to Ogden Projects, Inc., by Exxon Research and Engineering Co.

Until more information concerning the potential applicability of one or several of these methods to MWC testing has been developed, it is the judgment of the Work Group that methods for sulfur trioxide/sulfuric acid mist sampling and analysis must be selected on a case-by-case basis during discussions with the regulatory agency(ies) requesting these data.

5.2.2 Critical Features

Because it is not aware of satisfactory method validation data for measurement of sulfur trioxide/sulfuric acid mist in MWC emissions, the Work Group recommends that especially careful consideration be given to the design of a QA/QC protocol for any such testing on a case-by-case basis.

6.0 FORMALDEHYDE

6.1 METHOD DESCRIPTION

There are no standard EPA methods that are directly applicable to the determination of formaldehyde in MWC effluents. The procedure recommended by the NESCAUM Work Group for formaldehyde measurement is an MM5 train using a special XAD-2 resin that has been coated with 2,4-dinitrophenylhydrazine (DNPH) hydrochloride. During sampling, the formaldehyde is converted to its 2,4-DNPH derivative. The derivative is recovered by solvent desorption and analyzed by high performance liquid chromatography (HPLC).

An alternative method is use of the M5 train, with DNPH reagent in the impingers.

6.1.1 Sample Collection

Procedures for preparing the DNPH-coated XAD-2 are presented in an NTIS report, EPA Number 600/9-84-015, *Proceedings of the Ninth Annual Research Symposium on Incineration and Treatment of Hazardous Waste*. The relevant publication is Beltis *et al.*, *Stack Sampling and Analysis of Formaldehyde*.

The MM5 train is operated as described in Section 3.1 of this document. It is critical that the temperature of the gas stream entering the sorbent cartridge not exceed 20°C to prevent decomposition of the coated resin. Other critical features of the sampling are as described in Section 3.1.2 of this document. It is recommended that the formaldehyde train be run as a dedicated sample for formaldehyde determination.

6.1.2 Sample Analysis

The sorbent cartridge is desorbed using acetonitrile solvent in a Soxhlet apparatus. The resulting extract is concentrated to a volume of 10 mL using a Kuderna-Danish evaporative concentrator.

The HPLC analysis procedure is described in Kuwata *et al.*, "Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs as Their 2,4-Dinitriphenylhydrazones by High Performance Liquid Chromatography," *J. Chrom. Sci.*, 17, 264, May 1979. This procedure can also be applied to formaldehyde collected using M5 with DNPH impinger reagent. In that case, the aqueous reagent is extracted with chloroform, which is back-washed with 2N HCl and distilled water, concentrated to dryness, and redissolved in acetonitrile.

6.2 CRITICAL FEATURES

These procedures have been applied to only a limited number of full-scale combustion sources and not, to the Work Group's knowledge, on MWC tests. Formaldehyde sampling and analysis should, therefore, be regarded as a research and development activity. The rationale for recommending this relatively unvalidated procedure is that it is one of the few methods for formaldehyde that is compound-specific, rather than being a total aldehyde/ketone procedure (the MBTH and chromotropic acid procedures are for total carbonyls).

Many lots of XAD-2 resin (and many chemical laboratories) have relatively high background levels of formaldehyde contamination, which can result in positive interferences. Hence, the analysis of blank samples is critically important. (It is possible that alternative substrates to XAD-2, e.g., Tenax, may give lower background levels. If so, they should be substituted for the XAD-2).

6.3 QUALITY ASSURANCE AND QUALITY CONTROL PROCEDURES

6.3.1 Calibration

A minimum of five calibration solutions consisting of formaldehyde dinitriphenylhydrazone in acetonitrile and spanning the concentration range expected in the sample must be analyzed. The curve must not be force-fit through zero. A minimum of two calibration standards must be analyzed each day that samples are run.

6.3.2 Blanks

A method blank consisting of an unused, coated XAD-2 cartridge (or volume of DNPH impinger reagent) must be analyzed with each batch of samples. In addition, each lot of sorbent (or impinger reagent) must be checked for an acceptable background level prior to field sampling.

6.3.3 Replicate

A minimum of three stack gas sampling runs should be performed. Replicate determinations (reinjections of the sample extract into the HPLC system) should be performed on at least 10% of the samples or at least once on each batch of samples.

6.3.4 Spikes

With each batch of samples, at least one spiked sample must be analyzed. The spike should consist of a blank sorbent cartridge (or volume of impinger reagent) to which formaldehyde has been added at a level corresponding to the emission limitation specified in the permit (assuming a 1.1 m^3 stack gas sample).

6.4 DATA QUALITY OBJECTIVES

6.4.1 Limit of Detection

The detection limit for formaldehyde in the cited procedure is about 0.5 ng formaldehyde/20 µL of acetonitrile. Assuming an M5 or MM5 train stack sample volume of 1.1 m^3 and a final sample extract volume of 10 mL acetonitrile, this corresponds to an in-stack detection limit of about 0.25 $\mu g/m^3$. Based on data in the Report to Congress (EPA/530-SW-87-021b), the expected formaldehyde concentration in MWC stack gas is on the order of 100 $\mu g/m^3$ or higher; detection limits should, therefore, be adequate for MWC testing.

6.4.2 Accuracy

The recovery of formaldehyde from the spiked sample should be in the range of 60 to 100%. Results should not be corrected for recovery, but the percent recovery must be stated in the report.

6.4.3 Precision

The correlation coefficient for the calibration curve should be 0.990 or higher. Replicate HPLC analyses of the sample extracts should agree within ±10%. There is insufficient history of application of this method to MWC testing to allow a DQO for agreement among replicate stack gas samples to be established.

7.0 CITED REFERENCES

Alford-Stevens, A., T. A. Bellar, J. W. Eichelberger, and W. L. Budde. *Method 680. Determination of Pesticides and PCBs in Water and Soil/Sediment by Gas Chromatography/Mass Spectrometry*. U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory, Cincinnati, OH. November 1985.

Beltis *et al. Stack Sampling and Analysis of Formaldehyde*. In Proceedings of the Ninth Annual Research Symposium on Incineration and Treatment of Hazardous Waste. EPA 600/9-84-015, NTIS PB84-234525, 1984.

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Erickson, M. D. *Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Commercial Products and Product Wastes, Revision 2*. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC. EPA 560/5-85-010, NTIS PB86-109089 (1984a).

Erickson, M. D. *Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Air, Revision 2*. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC. EPA 560/5-85-011, NTIS PB86-109097 (1984b).

Erickson, M. D. *Analytical Method: The Analysis of By-Product Chlorinated Biphenyls in Water, Revision 2*. U.S. Environmental Protection Agency, Office of Toxic Substances, Washington, DC. EPA 560/5-85-012, NTIS PB86-109105 (1984c).

Kuwata *et al.*, "Determination of Aliphatic and Aromatic Aldehydes in Polluted Airs as Their 2,4-Dinitrophenylhydrazones by High Performance Liquid Chromatography," *J. Chrom. Sci.*, 17:264, May 1979.

U.S. Environmental Protection Agency, *Test Methods for Evaluating Solid Waste*, SW-846, Third Edition. November 1986.

Exxon, *Procedure for the Titrimetric Determination of Sulfur Trioxide and Total Sulfur Oxides in Flue Stack Emissions*. Personal communication from B. E. Hurst, Exxon Research and Engineering Company, P.O. Box 101, Florham Park, New Jersey 07932 to H. Von Dem Fange, Cooper Engineers, 1301 Canal Blvd., Richmond, California 94804-3555, October 8, 1985.

APPENDIX B

SELECTED DETAILED PROCEDURES FOR MEASUREMENT OF PCDDs AND PCDFs IN MWC STACK EMISSIONS

The detailed procedure descriptions presented in this appendix are intended to provide advisory guidance for selected sampling and analysis operations presented in Section 3.1.1 of the body of this document.

1.0 FIELD SAMPLE RECOVERY

At the completion of sampling, the probe and umbilical should be carefully removed from the train, the ends of the probe and the train should be capped with precleaned aluminum foil or glass caps, and the probe and train should be removed to a clean field or permanent laboratory for sample recovery. The recovery procedure for each train component is described below.

1.1 PARTICULATE CATCH

The filter should be carefully removed and folded to avoid loss of collected particulates and placed in a precleaned sample jar. The contents of the cyclone (if used) should also be transferred to the same jar.

1.2 FRONT HALF RINSE

The probe should be thoroughly brushed using a natural bristle brush with steel rod to recovery particulates. During brushing, the probe should be inclined and rinsed three times with methanol followed by three rinses with dichloromethane into a precleaned sample bottle. The front half of the filter holder, cyclone (if used), and connecting lines between the filter holder and probe should be similarly rinsed sequentially with methanol and dichloromethane into the same or a separate precleaned sample bottle.

1.3 BACK HALF RINSE

The back half of the filter holder, condenser, and connecting lines between the filter holder and the resin cartridge should also be rinsed three times with methanol following three rinses with dichloromethane into a precleaned sample bottle.

1.4 RESIN CARTRIDGE

The resin cartridge should be removed from the train, the ends capped with precleaned aluminum foil or glass caps, and the cartridge returned to the analysis laboratory intact.

1.5 FIRST IMPINGER

The water contained in the impinger should be measured gravimetrically or by pouring it into a precleaned graduated cylinder. Following this determination, the water should be poured into a precleaned sample bottle. The impinger should be rinsed three times with methanol followed by three dichloromethane rinses and the rinses added to the sample bottle. If the water was measured using a graduated cylinder, the cylinder should be similarly rinsed into the sample bottle.

Following recovery, all sample containers and the resin cartridge should be stored at 4°C or at wet ice temperatures and protected from light until analyzed. The remainder of the impingers should be recovered as specified in Method 5 for determination of the moisture content of the sample.

2.0 SAMPLE EXTRACTION AND CLEANUP

2.1 SAMPLE EXTRACTION

2.1.1 Solid Samples

The XAD-2 resin and particulates catch should be extracted with toluene or benzene in a single Soxhlet extractor. Pour the resin into a

pre-extracted cellulose thimble in the sample chamber of the extractor and rinse the resin cartridge with methanol followed by the extraction solvent (toluene or benzene) into the thimble. Add the filter to the thimble on top of the resin. If a cyclone was used, pour the cyclone catch onto the filter and resin and rinse the sample container as required, also into the sample thimble. If the probe rinse contains a noticeable amount of particulates, the rinse can be filtered through a pre-rinsed cellulose filter and the filter added to the extraction thimble. The MIS solution can be spiked before or after adding the MM5 filter to the thimble.

The combined solids sample should be extracted for approximately 16 h at a rate of about 3 cycles/hr. Following extraction, the extract should be concentrated to 5 mL using a rotary evaporator. Kuderna-Danish evaporative concentration can be used for benzene extracts.

2.1.2 Aqueous Components and Rinses

Aqueous and rinse components should be partitioned between water and dichloromethane. Pour the entire contents of the sample into an appropriate size separatory funnel. Spike the sample with the MIS solution unless the extract is to be combined with another spiked extract. If the sample is composed primarily of the train rinse solvents, add a sufficient amount of reagent water so that the dichloromethane is no longer miscible with the methanol and water, then separate the layers. Extract the aqueous layer with three portions of dichloromethane and combine the extracts. The combined extracts should be concentrated using Kuderna-Danish equipment.

2.2 EXTRACT CLEANUP

The extracts from the solids (resin and particulate catch) and rinses should be combined and concentrated to approximately 1 mL using nitrogen blowdown. At this point, approximately 15 µL of tridecane, hexadecane, or similar keeper should be added and the extract further evaporated to near dryness. The extract should be redissolved in 15 mL of hexane in preparation for cleanup.

The extract should be cleaned as described in Method 8280. The crude extract is initially cleaned by partitioning with 20% aqueous KOH, 5% aqueous NaCl, concentrated sulfuric acid, and 5% aqueous NaCl. The extract is then dried by passage through a column of anhydrous sodium sulfate and concentrated to 2 mL by Kuderna-Danish and nitrogen blowdown. Since the crude extract was previously concentrated using a keeper solvent, concentration to near dryness to remove all traces of toluene or benzene just prior to chromatography on alumina is not necessary.

The concentrated extract (in hexane) should be cleaned by chromatography on alumina and carbon columns as described in Method 8280. The collected toluene fraction from the carbon column should be concentrated to approximately 5 mL for storage awaiting GC/MS analysis.

Just prior to GC/MS analysis, an aliquot of the cleaned extract should be further concentrated to 25 µL in tridecane or hexadecane. The final concentration should be conducted as follows.

a. Dispense 25.0 µL of tridecane or hexadecane into a 1.0-mL conical Reacti-vial and mark the level of solvent on the vial;

b. Add 0.5 to 0.75 mL of the cleaned extract to the vial and concentrate to 25 to 50 µL;

c. Repeat the addition and concentration to quantitatively transfer the entire extract into the Reacti-vial (including rinses as required);

d. Concentrate to the mark or slightly below and make up to the mark with the keeper solvent; and

e. Spike the extract with the recovery internal standard (RIS) solution.

3.0 SAMPLE EXTRACT ANALYSIS

Sample extracts must be analyzed by GC/MS as described in Method 8280, SW-846 using a fused silica capillary column and selected ion monitoring (SIM) data acquisition.

3.1 GC/MS INSTRUMENTATION

The GC/MS system must provide sufficient chromatographic separation and a level of sensitivity sufficient to achieve the desired minimum detection limits for all subject PCDDs and PCDFs in the flue gas sample.

3.1.1 Gas Chromatograph

A high performance splitless injection system and fused silica capillary column are required. Column selection must consider chromatographic resolution of the analytes, but should also consider the run time required for acceptable resolution and the durability of the column. Several columns have been successfully used. Method 8280 recommends DB-5 (30 m), CP-Sil-88 (50 m), and SP-2250 (30 m) columns. An example column and temperature program that have been used for determining tetrachloro through octachloro PCDD and PCDF homologs is presented below.

Example GC Column and Conditions for PCDD and PCDF Homologs

Column: DB-5, 30 m
Initial Temperature: 200°C, 4 min
Temperature Program: 5°C/min to 330°C, 5-min hold
Approximate Analysis Time: 35 min

Determination of 2,3,7,8-TCDD and/or the 2,3,7,8-substituted PCDD and PCDF congeners requires demonstration of resolution of 2,3,7,8-TCDD from 1,2,3,4-TCDD with ≤ 25% valley. Hence, longer columns and slower temperature programs are typically required. Two example columns and conditions that have been used for determining the 2,3,7,8-substituted PCDD and PCF congeners are presented in Table B-1.

3.1.2 GC/MS Interface

The gas chromatographic column should be interfaced with the mass spectrometer by threading the exit end of the column directly into the ion source of the spectrometer. This avoids dead volume in connecting to a transfer line. If the column cannot be threaded into the source, a fused silica transfer line can be used.

3.1.3 Mass Spectrometer

The mass spectrometer must be capable of selected ion monitoring with sufficient sensitivity to achieve the target detection limits for PCDDs and PCDFs in the flue gas sample. The spectrometer must also be interfaced with a mass spectrometry data system to provide continuous data acquisition and storage during the GC/MS run and permanent data storage in machine-readable form. The required instrumental detection limits should be calculated from the target detection limits, the flue gas sample volume, and the final extract volume. If the extracts are split, the fraction of the total extract available for analysis must also be considered.

TABLE B-1. EXAMPLE GAS CHROMATOGRAPHIC COLUMN CONDITIONS FOR 2,3,7,8-SUBSTITUTED PCDD AND PCDF CONGENERS

Example 1

Column: DB-5, 60 m
Initial Temperature: 200°C, 2 min
Temperature Program 1: 5°C/min to 220°C, 16-min hold
Temperature Program 2: 5°C/min to 235°C, 7-min hold
Temperature Program 3: 5°C/min to 330°C, 5-min hold
Approximate Analysis Time: 60 min

Example 2

Column: DB-5, 60 m
Initial Temperature, 190°C, 1 min
Temperature Program 1: 5°C/min to 220°C, 16-min hold
Temperature Program 2: 5°C/min to 235°C, 7-min hold
Temperature Program 3: 5°C/min to 250°C, 18-min hold
Temperature Program 4: 5°C/min to 270°C, 7-min hold
Temperature Program 5: 5°C/min to 300°C, 24-min hold
Approximate Analysis Time: 95 min

The spectrometer must also be interfaced with a data system providing continuous data acquisition and storage during the GC/MS run. The software must be capable of producing chromatogram plots for the intensities of the selected ions.

The ions used to determine PCDDs and PCDFs are presented in Method 8280, SW-846. At least two ions should be used for each homolog.

3.2 SAMPLE ANALYSIS

PCDDs and PCDFs is sample extracts are quantitated using response factors normalized to the MIS compounds spiked prior to extraction. These relative response factors (RRFs) are determined by analyzing at least three levels of calibration solutions prior to sample analysis. The closest MIS analog should be selected for use with each native congener. The calibration solutions should contain the following.

a. A native congener representative of each PCDD or PCDF homolog to be quantitated, at one of the three calibration levels.

b. The MIS compounds at levels corresponding to that spiked into the samples, i.e., equivalent to 100% recovery.

c. At least one recovery internal standard compound (RIS), to be used to determine the recoveries of the MIS compounds, at a level similar to the MIS compounds.

An example of the compounds included in a calibration standard for determining 2,3,7,8-substituted PCDDs and PCDFs is presented in Table B-2. The levels of the native congeners in solutions should cover a 100-fold concentration range and the lowest concentration should be approximately 5 times the practicable detection limit. The RRFs of the native congeners should agree with a relative standard deviation (RSD) of $\leq$ 20% for all congeners. RRFs are also calculated for the MIS compounds normalized to the RIS compound and should similarly agree with 20%.

TABLE B-2. LIST OF ANALYTES, METHOD INTERNAL STANDARDS, SURROGATES, AND RECOVERY INTERNAL STANDARDS FOR DIOXIN/FURAN ANALYSIS

Analyte	Compounds in calibration standard	Method internal standard[a]	Recovery internal standard[b]
Tetra-CDD	2,3,7,8-TCDD	$^{13}C_{12}$-2,3,7,8-TCDD	$^{37}Cl_4$-2,3,7,8-TCDD or
Tetra-CDF	2,3,7,8-TCDF	$^{13}C_{12}$-2,3,7,8-TCDF	$^{13}C_{12}$-1,2,3,4-TCDD
Penta-CDD	1,2,3,7,8-PeCDD	$^{13}C_{12}$-1,2,3,7,8-PeCDD	
Penta-CDF	1,2,3,8,9-PeCDF	$^{13}C_{12}$-1,2,3,8,9-PeCDF	
Penta-CDF	2,3,4,7,8-PeCDF	$^{13}C_{12}$-1,2,3,7,8-PeCDD	
Hexa-CDD	1,2,3,4,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD
Hexa-CDD	1,2,3,6,7,8-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDD	1,2,3,7,8,9-HxCDD	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDF	1,2,3,4,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDF	1,2,3,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDF	2,3,4,6,7,8-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hexa-CDF	1,2,3,4,8,9-HxCDF	$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	
Hepta-CDD	1,2,3,4,6,7,8-HpCDD	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	
Hepta-CDF	1,2,3,4,6,7,8-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	
Hepta-CDF	1,2,3,4,7,8,9-HpCDF	$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	
Octa-CDD	OCDD	$^{13}C_{12}$-OCDD	
Octa-CDF	OCDF	$^{13}C_{12}$-OCDD	

[a] Added to sample prior to extraction.

[b] Added to sample at time of injection into GC/MS.

Once the calibration has been achieved, it is verified each day of sample analysis by analyzing the mid-level standard at the beginning and end of the day. The RRFs for the daily standards must be within 20% of the calibration RRFs, otherwise the recalibration is necessary. If 2,3,7,8-TCDD or all the 2,3,7,8-substituted congeners are to be determined, a column performance solution must also be analyzed each day to verify chromatographic separation between 2,3,7,8-TCDD and 1,2,3,4-TCDD. Separation must be achieved with ≤ 25% valley.

3.3 RESULTS CALCULATION

The concentrations of the native PCDDs and PCDFs are determined using their response factors relative to the MIS compounds. Results should be reported as mass of homolog or congener per sample volume, e.g., ng TCDD/dscm. Since an internal standard method is used, the quantities of native PCDDs and PCDFs determined are corrected for losses during sample extraction, extract cleanup, extract concentration, and other extract handling. The recoveries of the MIS compounds spiked into the samples prior to extraction are determined using RRFs relative to the RIS compound. The recoveries of the MIS compounds should be within the range of 50 to 150%. Recoveries outside this range may indicate problems in the analysis. Detection limits should be determined for each specific congener or homolog not detected using a response of 2.5 times the background noise signal at the appropriate retention time.